

THE  
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JOURNAL  
OF  
THE CHEMICAL SOCIETY  
OF  
LONDON.

EDITED FOR THE SOCIETY  
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VOL. I.

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## P R E F A C E.

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IN order to promote the more speedy and regular circulation of the communications made to the Society, amongst its members, the Council has resolved to publish the Memoirs and Proceedings, which up to this time have appeared at irregular intervals, in the form of a **QUARTERLY JOURNAL**.

It has been resolved, that Notices and Abstracts of the more important papers upon Chemical Subjects which may appear in foreign Journals, shall be appended to each number of this Quarterly Journal, and that the *January Number* for each year shall contain an alphabetical list of the heads of all Chemical Papers which have appeared during the year, both at home and abroad, up to the time of publication of the Journal.

DECEMBER 30, 1848.

PROCEEDINGS OF THE  
CHEMICAL SOCIETY  
UP TO THE TIME OF PUBLICATION OF THE JOURNAL.

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Nov. 20, 1848.—The following papers were read, “On the Ashes of Esculent Vegetables,” by John T. Herapath, Esq.

“Analyses of Black-Ash, Soda-Ash, &c.” by Frederick Muspratt, Esq.

A Note on the paper of Mr. Vaux, “As to the Presence of Traces of Copper and Lead in Coal,” by J. Philips, Esq.

December 4, 1848.—“On a Balance Galvanometer,” by W. S. Warde, Esq.

“Analysis of the Water supplied to the Highgate district,” by W. A. Mitchell, Esq.

“On the Action of Barytes on Salycilic Ether,” by G. Baly, Esq.

December 18, 1848.—John Thomas Cooper, Vice-President in the Chair. A paper was read by Dr. Hofmann, “On the Volatile Organic Bases,” Part IV.

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Nov. 1, 1847.

William Thomas Brande, Esq., President, in the Chair.

The following presents were announced to the Library of the Society : The last volume of the Transactions and 2 volumes of the Proceedings of the Society of Natural History of Vienna, presented by the Society ; the current numbers of the American Journal of Science ; the Journal of the Franklin Institute ; the Pharmaceutical Journal, the Chemical Gazette, and the Agricultural Journal, presented by their respective Editors.

The following communications were read :

*Upon the chemical composition of Pollen*, by THORNTON J. HERAPATH, Esq.—By treating the pollen of the red and white lily (*Lilium bulbiferum* and *candidum*) with water, alcohol, and ether successively, a number of matters, already described by other authors, were removed, leaving pollenin as a lemon-yellow coloured residue, possessing the properties usually accorded it, with these few exceptions. The pollenin from these sources was soluble without alteration in nitric acid, when too much heat was not applied, and water precipitated it unchanged from the acid solution. On boiling the solution in nitric acid, decomposition ensued, the tallow-like substance, mentioned by Berzelius, appeared upon the surface of the liquid, and no pollenin could then be precipitated by water ; no oxalic or carbazotic acids were found amongst the products of this decomposition. Starch was not detected in the pollen from the lily ; a peculiar colouring matter was found in that from the red, which did not exist in that of the white lily.

The author likewise examined the pollen from the *Cactus speciosissimus*, in which starch appeared to occupy the internal parts of the pollen granules. The amounts of pollenin yielded by 100 parts of these varieties of pollen, were as follows :

from <i>Lilium bulbiferum</i>	.	.	43·012.
„ <i>Lilium candidum</i>	.	.	36·936.
„ <i>Cactus speciosissimus</i>	.	.	46·575.

I. *On Cumidine; a new Organic Base. By EDWARD CHAMBERS NICHOLSON, Esq.*

The recognition of a close connection between the physical properties and chemical constitution of bodies, which has latterly attracted the attention of chemists, has chiefly been arrived at by comparing substances of corresponding series, which present a close and simple relation to each other. Our knowledge in this direction is, as yet, but limited, and certainly can only be extended by a careful comparison of the members of various parallel groups.

The beautiful relation, between the boiling point, and the number of equivalents of carbon and hydrogen of various compounds, which the researches of H. Kopp have pointed out, can only be verified and fully established, by a still more complete investigation of analogous substances.

It was in consequence of these considerations that Dr. Hofmann occasioned a series of experiments to be carried on in his laboratory, on the derivatives of cuminic acid, a substance which the researches of Gerhardt and Cahours have proved to be an analogue of benzoic acid, the products from which latter substance have been more completely studied than those from any other body.

As a part of these researches, some of which have already been communicated to the Chemical Society, I had undertaken the study of the derivatives of cumol; the bodies corresponding to nitrobenzol, dinitrobenzol, azobenzol, aniline and nitraniline. None of these bodies were known when I commenced this investigation: some time since, however, M. Cahours gave notice in a paper, "On the action of a mixture of sulphuric and nitric acids on several organic substances," that he was engaged with an investigation of the same subject.

In this notice, M. Cahours gives the composition of nitrocumol and dinitrocumol, and briefly mentions that these bodies are converted into basic substances by the action of reducing agents.

In consequence of this announcement, I refrain from a further prosecution of this subject, and will give here only the results I

have obtained, by examining the member, which in the cumol series, is the representative of aniline in the benzol series.

#### PREPARATION OF CUMIDINE.

The preparation of this base from cumol is exactly analogous to that of aniline from benzol.

Cumol was treated with fuming nitric acid until it was entirely dissolved, heat being evolved during the reaction, and a large quantity of red vapours given off. On the addition of water, a dark red oily body precipitated, which was nitrocumol. An alcoholic solution of this substance was saturated first with ammoniacal gas, and then with hydrosulphuric acid. After the lapse of a few days, the liquid lost the smell of that gas, and a large quantity of sulphur separated; it was again treated with hydrosulphuric acid and distilled. This process was continued until the whole of the nitrocumol was decomposed. Alcohol and sulphide of ammonium having been removed by the last distillation, the residue in the retort was dissolved in hydrochloric acid, filtered from a small quantity of sulphur, and evaporated, until upon cooling, the whole became a crystalline mass.

These crystals constituted the hydrochlorate, of the representative in the cumol series, of aniline and toluidine in their respective series, and for which I propose the name of "Cumidine." On treating the boiling aqueous solution of this salt with caustic potash, the base immediately separated in oily drops, which collected in an uniform layer, on the surface of the fluid. The purification of the base was very simple. The distillate was saturated with a concentrated solution of oxalic acid, and evaporated to dryness:—the residue dissolved in boiling alcohol, and treated with animal charcoal. On cooling, the oxalate was deposited in colourless crystalline plates, which were absolutely pure. The solution of this salt in water was decomposed by hydrate of potash. On separating the oily liquid, by means of a pipette, and distilling rapidly, the base was obtained pure and colourless; traces of water having been previously removed by contact with potash.

#### COMPOSITION OF CUMIDINE.

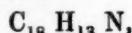
The preparation and properties of this base, being analogous to those of aniline and toluidine, left no doubt in my mind as to its composition. Nevertheless, I have made the following determination of carbon, hydrogen and nitrogen, which proves that cumidine, like the above-mentioned substances, is free from oxygen.

I. 0·2017 grm. of substance, burnt with oxide of copper, gave 0·5902 grm. of carbonic acid and 0·1755 grm. of water.

II. 0.4944 grm. of substance, burnt in an atmosphere of carbonic acid gave 45 c. c. of moist nitrogen. Bar. 768.9 mm. (30.27 in.) Therm. 18° C. (64.5 F.) which calculated for 100 parts, give :

	I.	II.
Carbon . . . . .	79·82	"
Hydrogen . . . . .	9·66	"
Nitrogen . . . . .	"	10·67

### **Agreeing exactly with the formula:**



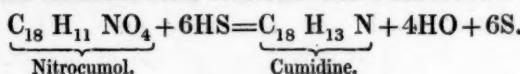
as will be seen when the numbers are placed in comparison with the calculated numbers:

		Theory.	Experiment.
18 equiv. Carbon . . . .	108 . .	80·00 . .	79·82
13 „ Hydrogen . . . .	13 . .	9·63 . .	9·66
1 „ Nitrogen . . . .	14 . .	10·37 . .	10·67
1 „ Cumidine . . . .	135 . .	100·00 . .	

To prove the accuracy of the formula for this base, and control its atomic weight, I submitted the platinum double compound to a careful analysis. Two determinations, which I shall hereafter mention in detail, gave 28.85 and 28.93 per cent of platinum, the corresponding numbers to which closely agree with the calculated atomic weight.

	Mean.	Theory.
I. Atomic weight by experiment .	135.82	135.00
II. " " "	134.82 } 135.32	

The formation of cumidine from nitrocumol, is analogous to that of aniline and toluidine from nitrobenzol and nitrotoluol:



## PROPERTIES OF CUMIDINE.

This body, as previously stated, is obtained in the form of a slightly yellowish oil, dispersing and refracting light in an eminent degree, and possessing a peculiar smell and burning taste. In a mixture of ice and salt, it solidifies to a mass of square plates, which rapidly disappear when the temperature increases. It seems, that under peculiar circumstances, this body becomes crystalline at ordinary temperatures. On one occasion, in the winter, I obtained this body in beautiful square plates, resembling those obtained when

the oil is exposed to a frigorific mixture, and which have continued solid up to the present time. It is also well known that toluidine and napthalidine often remain liquid for a considerable period.

Cumidine is very soluble in alcohol, ether, pyroxilic spirit, bisulphide of carbon, and the fatty oils. Water also dissolves it in small quantity. The base has no action on reddened litmus or turmeric papers. It evaporates but slowly at ordinary temperatures, and leaves a stain on paper, which disappears after some time. Cumidine is lighter than water, its spec. grav. being 0·9526.

I was very anxious to ascertain the boiling point of cumidine :— in two experiments made with different specimens, the liquid boiling in contact with a coil of platinum wire, and nearly an ounce distilling over, the thermometer became stationary at 225° C. (437° F.) Bar. 761·1 mm. (29.965 in.).

On comparing this result with the number calculated by H. Kopp's empirical rule, a considerable discrepancy is obvious.

If we take as a starting point, the boiling temperature of aniline, which has lately been verified in several experiments by Dr. Hofmann, we obtain the following calculated numbers, for the series of bases between aniline and cumidine :

	Theory.	Experiment.
Aniline . . . . .	182° C. . . . .	182° C. Hofmann.
Toluidine . . . . .	201 " , .	198 " Muspratt and Hofmann.
Unknown base . . . . .	220 " . . . "	" "
Cumidine . . . . .	239 " . . . 225	" Nicholson.

Cumidine, when recently distilled, is nearly colourless, but on a few minutes' exposure to the air, rapidly changes, first to a yellow, and finally to a dark red colour; this alteration takes place with greater rapidity at high temperatures. Its vapour is highly inflammable, burning with a yellowish flame, and depositing large quantities of carbon.

Cumidine, like aniline and toluidine, imparts an intense yellow colour to fir-wood, but it does not afford the beautiful reaction with hypochlorite of lime which characterizes the former base.

The basic properties of this substance, although very feeble, are rendered obvious by its comportment with the salts of weak mineral oxides. An aqueous solution of cumidine separates hydrated sesquioxide of iron from the sesquichloride, but gives no precipitate with the salts of zinc or alumina.

#### COMPOUNDS OF CUMIDINE.

The basic character of this substance is moreover exhibited in the

extraordinary facility with which it forms crystalline compounds with acids; a property in which it also resembles aniline and toluidine. All these salts, except some metallic double compounds, are colourless when recently prepared; but some of them, especially when moist, or exposed to a high temperature, assume a pinkish hue. They are soluble in water, and more so in alcohol. When decomposed by the caustic alkalies, the base separates in dark oily globules if the solution be concentrated; if dilute, as a white curdy precipitate. All the salts of cumidine, like those of aniline, are anhydrous. They are acid to litmus paper. When rapidly boiled in water for some time, they are partially decomposed, the base volatilising.

#### SULPHATE OF CUMIDINE.

I obtained this salt by dissolving the base in boiling dilute sulphuric acid; upon cooling, the whole became a crystalline mass. When dissolved in water, and decolourised by animal charcoal, crystals of perfect purity were obtained on cooling.

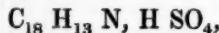
This salt is only slightly soluble in water, but more soluble in alcohol; it is inodorous, but possesses a disagreeable bitter taste. At  $100^{\circ}$  C. ( $212^{\circ}$  F.) it emits the odour of the base, but is not otherwise altered in properties, except that it assumes a faint pink tint.

I. 0·2357 grm. of substance, burnt with oxide of copper, gave 0·5070 grm. of carbonic acid and 0·1687 grm. of water.

II. 0·2994 grm. of substance, precipitated with chloride of barium, gave 0·1902 grm. of sulphate of barytes, which quantities accord with the following composition in 100 parts :

	I.	II.
Carbon . . . . .	58·66	"
Hydrogen . . . . .	7·94	"
Sulphuric acid . . . . .	,,	21·77

corresponding to the formula :



as is seen by the following calculation :

	Theory.	Experiment.
18 equivs. of Carbon . . . . .	108 . . .	58·70 . . . 58·66
14 " Hydrogen . . . . .	14 . . .	7·60 . . . 7·94
1 equiv. of Nitrogen . . . . .	14 . . .	7·61 . . . ,
1 " Oxygen . . . . .	8 . . .	4·35 . . . ,
1 " Sulphuric acid . . . . .	40 . . .	21·74 . . . 21·77
1 " Sulphate of cumidine . . .	<hr/> 184	<hr/> 100.00

## NITRATE OF CUMIDINE.

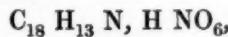
This salt is obtained by gently heating the base with dilute nitric acid. On cooling, the fluid becomes filled with long needle-like crystals, which are colourless, if the acid be not too concentrated, and are otherwise of a reddish tint.

It is soluble in water and alcohol, and is not decomposed at a temperature of  $100^{\circ}$  C. ( $212^{\circ}$  F.).

I. 0.3231 grm. of substance, burnt with oxide of copper, gave 0.6460 grm. of carbonic acid and 0.2145 grm. of water, which yield the following numbers per cent :

Carbon . . . . .	54.52
Hydrogen . . . . .	7.37

agreeing with the formula :



as is seen by the following calculation :

	Theory.	Experiment.
18 equivs. of Carbon . . . . .	108 . . .	54.54 . . . 54.52
14 . . . Hydrogen . . . . .	14 . . .	7.07 . . . 7.37
2 . . . Nitrogen . . . . .	28 . . .	14.15 . . . "
6 . . . Oxygen . . . . .	48 . . .	24.24 . . . "
1 equiv. of Nitrate of cumidine . . .	198	100.00

## HYDROCHLORATE OF CUMIDINE.

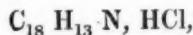
The base combines directly with hydrochloric acid, with the evolution of heat. By re-crystallization from water or alcohol, the salt is obtained in large well-formed prisms, perfectly white and inodorous. If moist or exposed to the air, it assumes a pink colour. It is not altered at a temperature of  $100^{\circ}$  C. ( $212^{\circ}$  F.), but at a higher temperature it melts and sublimes.

I. 0.1810 grm. of substance, burnt with chromate of lead, gave 0.4178 grm. of carbonic acid and 0.1360 grm. of water.

II. 0.3908 grm. of substance, precipitated with nitrate of silver, gave 0.3267 grm. of chloride of silver, which, calculated for 100 parts, is equivalent to :

	I.	II.
- Carbon . . . . .	62.94	"
Hydrogen . . . . .	8.34	"
Chlorine . . . . .	"	20.67

agreeing with the formula :



as will be seen by a comparison with the following calculated numbers:

	Theory.	Experiment.
18 equivs. of Carbon . . . . .	108 . . .	62.97 . . 62.94
14     ,     Hydrogen . . . . .	14 . . . .	8.17 . . 8.34
1 equiv. of Nitrogen . . . . .	14 . . . .	8.17 . . ,
1     ,     Chlorine . . . . .	35.5 . . .	20.69 . . 20.67
1     ,     Hydrochlorate of cumidine	171.5	100.00

Cumidine, when added to a boiling aqueous solution of oxalic acid, dissolves, and upon cooling, a salt crystallizes in beautiful pearly tables, which are difficultly soluble in water, but more so in alcohol.

I have made several analyses of this substance, and from the great difference in the numbers obtained, there remains no doubt that it is a mixture of the neutral with an acid oxalate. The small amount of substance at my command, has prevented me from separating these two bodies in a state of purity.

#### CUMIDINE AND BICHLORIDE OF PLATINUM.

This beautiful compound is obtained when an excess of bichloride of platinum is added to a hot solution of hydrochlorate of cumidine in water. Upon cooling, the compound is deposited in long yellow needles, which, after washing with a small quantity of water, are perfectly pure. This substance is decomposed when boiled with water. Its deportment with alcohol and ether is very singular. On adding a few drops of alcohol to a large quantity of this substance, it immediately dissolves, and after a short time, is precipitated in the form of a dark red oil, which, after evaporation of the alcohol, solidifies to a mass of crystals, of a magnificent orange-yellow colour. At a temperature of 100° C. (212° F.) it becomes rather darker in colour, but is not otherwise altered in properties. At a higher temperature it is decomposed into hydrochlorate of cumidine, which sublimes, and metallic platinum.

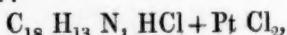
I. 0.3468 grm. of substance, burnt with chromate of lead, gave 0.3985 grm. of carbonic acid and 0.1400 grm. of water.

II. 0.4793 grm. of substance gave 0.1383 grm. of platinum.

III. 0.4967 grm. of substance gave 0.1437 grm. of platinum, which quantities accord with the following composition per cent :

	I.	II.	III.
Carbon . . . . .	31.33	"	"
Hydrogen . . . . .	4.48	"	"
Platinum . . . . .	"	28.85	28.93

and with the formula :



as may be seen by the following calculation :

	Theory.	Experiment.
18 equivs. of Carbon . . . . .	108 . . .	31·65 . . 31·33
14 " Hydrogen . . . . .	14 . . .	4·12 . . 4·48
1 equiv. of Nitrogen . . . . .	14 . . .	4·12 . . "
3 equivs. of Chlorine . . . . .	106·5 . . .	31·21 . . "
1 equiv. of Platinum . . . . .	98·68 . . .	28·90 . . 28·89
1 " Chloride of platinum and cumidine . . . . .	341·18 . .	100·00

I have not examined the other salts of this base, and shall only remark, that the hydrobromate, hydriodate, hydrofluate, metaphosphate, phosphate, acetate and tartrate, are immediately produced, when these acids are brought into contact with anhydrous cumidine. The hydriodate of cumidine seems to be the most soluble of its compounds.

Besides the simple salts mentioned, cumidine forms a great number of double compounds.

Bichloride of palladium produces a yellow precipitate, very similar in appearance to the platinum salt; it is soluble in water and alcohol, and crystallizes from the latter solvent in yellow needles.

An alcoholic solution of this base produces a violet precipitate with sesquichloride of gold, rather darker in colour than ferrocyanide of copper. It is soluble in alcohol, to which it imparts an intense colour.

Nitrate of cumidine combines with nitrate of silver, and forms a beautiful compound, crystallizing in long needles, which are soluble in water and alcohol without decomposition.

An alcoholic solution of cumidine produces with chloride of mercury, a white granular precipitate, which is decomposed by boiling water, with the formation of a yellow powder. With cyanide of mercury, cumidine also gives a crystalline precipitate.

Sulphate of copper produces a beautiful grass-green precipitate, in an alcoholic solution of the base, which is insoluble in water and alcohol.

#### PRODUCTS OF THE DECOMPOSITION OF CUMIDINE.

The great number of changes which oil of cummin undergoes before its conversion into cumidine : the treatment of the oil with hydrate of potash, in order to separate the cymol and to convert the cuminol into cuminic acid : the distillation of this acid with caustic lime, to procure cymol : the conversion of the cymol into

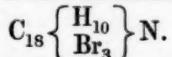
nitrocumol, by fuming nitric acid : and finally, the reduction of nitrocumol by hydrosulphuric acid, render the preparation of this base, in any quantity, a long and laborious process. In consequence of this difficulty, I could but briefly study the products of its decomposition.

Potassium, when heated in the vapour of cumidine, is converted into cyanide of potassium.

Concentrated nitric acid dissolves the base with a beautiful purple colour. On adding water to the solution, a flocculent precipitate is produced, which partakes of the character of an acid.

Dry chromic acid acts very powerfully on cumidine ; great heat is evolved, but the base does not inflame like aniline.

On treating cumidine with bromine, a violent action ensues, with the disengagement of heat and evolution of hydrobromic acid. The base is converted into a solid grey mass, which is soluble in alcohol and ether, but insoluble in water, and crystallizes from the former solvents in long white needles. The great analogy in the properties and in the mode of formation of this body to those of tribromomaniline, render it very probable that it is tribromocumidine :



When treated with a mixture of hydrochloric acid and chlorate of potash, the base is powerfully attacked and converted into a brown viscid mass, which had exactly the smell of chlorophenissic acid. When boiled in alcohol, it partially dissolves, and leaves a crystalline substance.

Aniline, when treated in a similar manner, yields, as is known, a mixture of chloranil and chlorophenissic acid ; whether the products obtained in the decomposition of cumidine are identical with those of aniline, or whether they only represent these products in the cumol series, has to be decided by further experiments, which I soon hope to undertake.

Cumidine also produces a class of substances analogous to the amides and anilides.

The base, when exposed to an atmosphere of phosgene gas, immediately solidifies, with the evolution of heat ; when washed with water to free it from hydrochlorate of cumidine, and then dissolved in boiling alcohol, it deposits on cooling, large crystals, very similar in appearance to nitrate of potash.

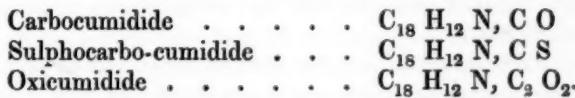
A mixture of bisulphide of carbon and cumidine, after the lapse of a few hours, evolves a large quantity of hydrosulphuric acid ; upon the addition of water, an oily body separates, which soon solidifies to

a crystalline mass. It is soluble in boiling alcohol, from which it is deposited in colourless needles.

These two latter substances are evidently carbo-cumide and sulphocarbo-cumide, corresponding to carbanilide and sulpho-carbanilide, lately described by Dr. Hofmann.

Oxalate of cumidine, when submitted to dry distillation, yields a crystalline substance, which is but difficultly soluble in water, and shows in every respect the comportment of oxicumide.

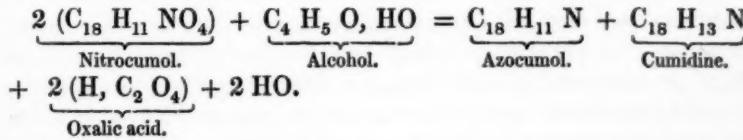
I have not made an analysis of these bodies, but there is little doubt that their composition may be represented by the following formulæ :



Messrs. Muspratt and Hofmann, in their paper on Toluidine, have proved that the formation of azobenzol, by the action of an alcoholic solution of hydrate of potash on nitrobenzol, is always accompanied by a simultaneous production of aniline. I was anxious to ascertain, whether nitrocumol would undergo an analogous metamorphosis.

On distilling an alcoholic solution of nitrocumol with caustic potash, a violent reaction ensued, and a deep red coloured oil collected in the receiver, which perfectly resembled azobenzol, before it has solidified ; in the latter stage of the process, a large quantity of cumidine passed over ; the residue in the retort contained considerable quantities of oxalate of potash.

The formation of these substances is accompanied and, as it seems, preceded by others ; but the final reaction may be represented by the following equation :



These experiments have been carried on in the laboratory of the Royal College of Chemistry ; and I cannot refrain from expressing my greatest thankfulness to Dr. Hofmann, for his superintendence and advice during their prosecution.

II. *An account of some experiments with Voltaic Couples immersed in pure water and in oxygenated water, by MR. RICHARD ADIE, of Liverpool.*

In the present communication, it will be my endeavour to trace a little further the line of demarcation between water, and oxygenated-water-voltaic actions, the existence of which was proved in the paper submitted by me last session for the consideration of the Society; an attempt will also be made to prove, that where a voltaic current is developed by two similar pieces of an oxidizable metal, the negative plate in such an arrangement is in reality the oxide of the metal.

In the trials described in the former paper, when zinc and iron acted as the positive elements of couples excited by boiling water, the galvanometer showed that the difference between them was only one of degree. With zinc, after long boiling, the galvanometer was deflected  $20^{\circ}$ , and with iron  $7^{\circ}$ , from which I was led to think, that although iron was usually held incapable of rusting in pure water, it might, like zinc, possess the power of slowly decomposing water, but that the quantity of oxide formed in this manner was so small, that it had heretofore escaped notice,—a view which is strengthened by a remark often made by other observers, that decomposition of water probably occurred during the ordinary rusting of iron, because ammonia was always found in the rust or hydrated oxide.

The experiment in which zinc and copper elements decomposed water in a hermetically sealed tube, occupied so long a time, that I despaired of obtaining any notable effect with iron, unless a large surface was brought into action. For this purpose, some iron was reduced from the red oxide by a stream of hydrogen; the precautions necessary for obtaining the metal in the state of greatest subdivision (the pyrophoric form), were carefully observed, and to prevent the spontaneous combustion to which I found the iron liable, the tube in which the metal had been reduced, was filled with water as soon as the temperature would permit. Iron, subdivided in this manner, was placed with distilled water in two tubes of hard glass; these tubes were then heated to the boiling temperature, and hermetically sealed. A third tube was similarly prepared, in which a surface of 45 inches of bright polished iron wire was substituted for the pyrophoric iron.

The woodcut, Fig. 1, represents the form of the tubes employed. *A* is the tube filled with water and iron, *BC* is a capillary portion

drawn out by the blow-pipe after the metal is inserted, and is sealed at *C*.

FIG. 1.



When the tubes are closed, the water on cooling leaves a space, which at first is only filled with aqueous vapour; but should any gas be generated, a portion of it will collect in that part. After three days had elapsed from the date of sealing, part of the atmosphere of the space left by the cooling of the water was driven into the capillary termination *BC*, where after resting for some hours, its bulk was registered by a mark at *B*, with a view to use this as a gauge for indicating change of pressure in the interior of the tube. The experiment was conducted in a room with a northern aspect, where the temperature was very steady, about 60° F. At the end of ten days, the gauges of the two tubes containing pyrophoric iron, gave decided evidence of an increase of pressure; and shortly afterwards, the gauge in the tube containing iron wire gave a similar indication.

From this time, the pressure in all the three tubes continued regularly to increase, and at the expiration of a month, one of them, containing pyrophoric iron, was opened, and the gas having been transferred to a detonating tube, was exploded with oxygen. At the end of two months, the gas from the cell containing the iron wire was likewise detonated with oxygen.

A portion of the finely divided iron was now taken from the hard glass tube, and having been repeatedly washed, was placed with pure water in a tube of ordinary flint glass. A second portion of the iron had a plate of platinized platinum associated with it in another tube. Both the gauges exhibited after a few days, indications of a gradual disengagement of gas.

These experiments clearly establish the fact that iron is capable of slowly decomposing water at ordinary temperatures. I believe if iron and water could be brought together, perfectly free from oxide of the metal or from oxygen gas dissolved in the water, that no decomposition could ensue; but this is a condition that cannot be attained in practice. Where iron forms the positive element of a couple excited by rain water, the oxygenated-water action and the

decomposition-of-water action, will exist together, the first of these being by far the more active.

If we ascend the scale of metals towards those which are less oxidizable, voltaic elements can be formed from one metal, which give rise in oxygenated water to a notable voltaic action. With copper as a positive element, I expected to get an effect due solely to oxygenated water, but I thought it better to subject the copper in the first place to the same series of experiments in which both iron and zinc had decomposed water.

A pair of copper and platinum plates, in oxygenated water at a temperature of 60° F., deflected the needle of the galvanometer . . . . . 5°

On heating the water nearly to the boiling point, the deflection amounted to . . . . . 50°

After 1½ hours' boiling, it was only . . . . . 1°

In this experiment, after thorough boiling, there remained merely a trace of voltaic action.

Some copper was precipitated in a subdivided form by a battery, from solutions of the chloride and sulphate, and the metal, after having been thoroughly washed, was placed with pure water in sealed tubes of flint glass, in the same manner as has been already detailed in the case of iron. After the tubes had been kept for three months at ordinary temperatures, their respective gauges showed no trace of the disengagement of gas. One of the tubes containing copper precipitated from the sulphate, was then digested for three weeks, at a temperature approaching that of boiling water. There was no appearance of action upon the copper, nor was there any gas evolved, but the water and the constituents of the flint-glass had undergone an extensive alteration. The water, though still transparent, was strongly alkaline to test-paper and even to the skin. The glass was quite opaque, in consequence of the formation of a thick coating of white enamel, and deeply corroded in parts where the enamel was scraped off. The enamel tested by the blow-pipe, gave evidence of lead, but none of copper. In the same bath were pieces of flint-glass, filled with oils and wax, also hermetically sealed, and in these the glass appeared unchanged at the end of three years' digestion.

At the same time that the tubes containing copper were prepared, similar tubes containing lead, tin, bismuth, and antimony were tried; they, however, have given no signs of the evolution of gas.

These results accord with the prevalent opinion, that copper does

not possess the power of decomposing water. Yet two similar pieces of this metal act as a voltaic couple when the one is more rapidly oxidized than the other. Two lengths of copper wire, of the same dimensions as the zinc and iron wires, represented at Fig. 2 of the last set of experiments, were placed in a stream of water during summer, at a period when the weather was steady and the surface-level of the stream was nearly stationary. The circuit between the plates was completed in the usual manner, with a small decomposing cell intervening, containing copper poles and a solution of sulphate of copper. In this case I found a steady precipitation of metallic copper, which at the end of three weeks, made a difference between the weight of the poles of  $\frac{1}{5}$ th of a grain, or the weight of metal precipitated was  $\frac{1}{10}$ th of a grain.

In my first communication, I referred to the sheathing of a ship as proof that the pieces of metal in a stream waste away in proportion to the rapidity of the current. With two pieces of copper in a stream, the analogy is yet more close. In still water I found the surface of the metal covered with large stains of black oxide, while on the metal exposed to the current, there was a general covering of a very thin film, of a dull green colour. In sheathing ships, copper of three degrees of thickness is applied to the same hull; the places in the fore part of the vessel are sheathed with the stoutest plates, and about the stern with the thinnest; experience having long ago shown that thinner metal on the parts about the stern, where the water is comparatively still, will endure as long as the stout metal on those parts where the water exerts greater friction. Connected with this subject, it may be further worthy of remark, that when the difference between the relative parts of the sheathing of a ship, which develops a notable voltaic action, is wanting, the copper fails completely to preserve the ship's bottom from fouling. This I have seen practically proved in the case of the light ships anchored near the entrance to the channels of the port of Liverpool, where they are exposed to the action of the tides and to the agitation of the Irish Sea. On one of these vessels, brought into dock for repair, the whole surface of the copper was covered, to a thickness of two inches, with marine plants and animals. From this it would appear, that the voltaic action, such as I have noticed in the experiment with copper wire in a stream, performs a part in preventing vegetation on the ship's bottom.

On examining the sheathing of a vessel just returned from a voyage, and noticing the dark red hue of the copper on those parts which are exposed to the currents of water produced by the sailing

of the ship, as contrasted with portions so placed as to be in comparatively still water, and which are coated with the green-coloured carbonate of the oxide of copper, few would hesitate to say that the bright part acted as a negative or platinode element, and corresponded with a piece of metal in the rapid part of a stream. In looking at copper in this state, I have hitherto considered that it owed its platinode action to its clean metallic surface; but this view I now believe can be shown by experiment to be incorrect; the active platinode is an oxide of copper, of which there is a continuous supply in the nascent state on the surface of the metal when exposed to a current of oxygenated water.

I selected silver as the metal best suited for the examination of the nature of the active platinode surface in oxygenated-water-voltaic actions. In the Edin. Phil. Journal, vol. XXXIX, p. 330, I have detailed some experiments with silver plates, to which I again returned. Two pieces of pure silver foil, placed in a horizontal position and connected with a delicate galvanometer, gave no action when immersed in oxygenated water; with oxide of silver strewed on one of the plates, a notable current, sufficient to precipitate metallic silver, was obtained. The oxide acted as a negative pole, and became coated with a film of a lilac or blueish leaden hue; but the tendency to this change was much modified by conditions attending its preparation, such as the temperature at which the oxide was washed and dried. When pale coloured oxide of silver is long boiled in pure water, the colour darkens, and I have generally found this dark coloured oxide most active as a platinode.

Oxide of silver, enclosed with pure water in a glass tube, undergoes no change; exposed in the tube to the sun's rays, it darkens in the same manner as if it were exposed to the atmosphere. After being darkened by light, the pale lilac colour appeared in a slight degree during night on the surface of the oxide, in a hermetically sealed tube, although no change could be perceived until the rays of the sun had been employed.

When the sun's rays fall on the oxide of silver, while it forms the negative portion of a voltaic couple, the needles of the galvanometer recede, and the colour of the oxide darkens rapidly; on the positive plate the sun has little influence.

In the arrangement for obtaining a voltaic action from silver elements, it was necessary to add some of the ready-formed oxide of the metal, which gradually changed colour on the surface exposed to the oxygenated water, and formed the negative element of the couple. The nature of this change appeared to me to be of

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importance, for shewing the action of metallic oxides as negative elements. The question I sought to determine was, whether the alteration noticed on the surface of the negative element, was due to the oxide of silver absorbing or parting with oxygen. The action of the sun's rays on the negative plate covered with oxide of silver diminished the voltaic effect, and as the solar light tends to reduce silver from its oxide, I inferred that the change observed on the surface of the negative element could not arise from a reduction of the oxide, for had it been so, the sun's rays should have increased the action of the couple. Again, in order to ascertain whether the oxide of silver, in assuming a pale hue, was absorbing oxygen, some oxide of silver was placed on filter-paper, and a jet of steam made to play on its surface for thirty minutes, without producing any change of colour. A jet of dry oxygen gas was directed in a similar manner on to dry oxide of silver without altering it. Then a jet of oxygen was made to play on moistened oxide of silver, when a light coloured stain appeared round the spot where the oxygen struck the oxide; careful washing, so as not to intermingle the particles of the oxide, did not remove the stain. The experiment was several times repeated, and a lapse of from ten to fifteen minutes was found sufficient to produce the stain, which was obtained both on the pale and darker coloured oxide. It is upon this experiment that I rely for proof that the change to a light colour on the surface of the oxide of silver is due to the production of a higher state of oxidation; and as the sun's rays rapidly destroy the light colour, and at the same time check the action of the plate as a negative element of a couple, *I infer that it is this compound on the surface of the brown oxide which is the real negative part of the arrangement*, while on the positive side, there is a slow oxidation of the bright silver.

To test the view of the oxide of a metal acting as a platinode, a piece of zinc was cut into two halves, one of these was roasted till its surface was covered with oxide, and then formed into a couple with the bright piece; on immersing these in water, the galvanometer indicated the oxidized surface to be negative. Similar results were obtained with couples of iron, formed of bright iron associated with a rusted piece, or a portion oxidized by heat; also from bright and oxidized copper, and from lead. In still water, the effect from these couples is, as might be expected, of short duration; oxide in a nascent state is soon developed on the bright surface to counterbalance the oxide opposite; but the development of a current can be made continuous if means be taken to form oxide more rapidly on one surface than on the other, of which the several experiments

stated afford examples, the plate most rapidly oxidized being negative.

I have always looked on oxygenated-water-voltaic couples, and the well known gas battery of Mr. Grove, as similar in their nature, the hydrogen of the gas battery supplying the place of the positive element; if we may hold that in an oxygenated-water action the negative element is the oxide of a metal, and that the action is of longer duration where there is a continuous supply of the oxide on the negative side in a nascent state, the extension of this principle to the gas battery would give nascent water as the negative element in Mr. Grove's arrangement.

Should the view I have been led, by the experiment on oxide of silver to adopt, stand the test of time, it will reconcile the action of couples formed of oxidizable metals with a general principle, which was suggested to me in examining thermo-electric actions; namely, *that in all electrical arrangements, the current passes from the side which is changing, towards that which is the more stationary.*

Where there are exceptions to this law among the more complicated batteries, I am now inclined to hope that they, when fully examined, will, like the oxygenated-water actions, become reconcileable to it; for at one time, I looked on the metal in a stream wasting away through rapid oxidation, and yet acting as a negative element, as in direct contradiction to this law; but now, the experiments show that it is not the metal that is the platinode, but a compound formed on its surface; and the more rapid the formation of the oxide on the negative side, by a supply of oxygen as in Grove's battery, or by a very swift stream of surface water, then the action of the couple increases in like proportion.

Nov. 15, 1847.

The President in the chair.

Resolved, having been proposed by the Council at the previous meeting, in accordance with Law 6, that an admission fee of £2 be required from members elected into the Society after the 30th day of March, 1848.

Taylor's Calendar of the Meetings of Scientific Bodies for 1847 and 1848, were presented by the Editor.

The Hon. and Rev. S. W. Lawley was elected a member of the Society.  
The following communications were read:

*On the Specific Heat of Bromine*, by THOMAS ANDREWS, M.D., M.R.I.A.—Bromine being the only liquid member at ordinary temperatures of the class of bodies to which it belongs, it appeared important to ascertain

its specific heat with reference to the law of Dulong and Petit. The low temperature at which bromine boils, and its feeble specific heat, rendered the determination of the latter difficult. The method adopted was to heat bromine, contained in a small glass flask, to about 10° C. (18° F.) below its boiling point, by means of a water-bath, which was maintained at a very steady temperature. It was then quickly transferred into a glass tube, which had been previously immersed in a copper vessel filled with water, and the increment of temperature in the water was carefully observed. The details of the experiment are the same as those usually followed in such investigations. The bromine employed was carefully purified, and its purity tested by ascertaining its atomic weight, from the silver salt, previous to the experiment. It boiled at a temperature of 58° C. (137.5° F.) under a pressure of 29.9 inches. In the experiments the temperature of the air was about 11 C°. (52° F.), and the bromine was heated to about 45° C. (113° F.). Br. represents the weight of the bromine; T the increment or gain of heat of the water; T' the heat lost by the bromine; and Sp. H. the specific heat.

I.	II.	III.	IV.	V.
Br. 25.08 grms.	26.13 grms.	24.98 grms.	24.69 grms.	24.48 grms.
T 1°.208 (C.)	1°.315 (C.)	1°.263 (C.)	1°.213 (C.)	1°.184 (C.)
T' 32°	32°	32°.7	31°.9	32°.4
Sp.H. 0.1053	0.1097	0.1083	0.1078	0.1044

Mean specific heat 0.1071.

Dr. Andrews concludes from these results that, in accordance with the views of Berzelius, the atomic weight usually ascribed to bromine in this country, as also those of the elements of the class to which it belongs, should be halved, in which case, silver being taken at 1350, bromine, from the author's experiments, would be  $\frac{999.4}{2}$  or nearly  $\frac{1000}{2}$ , and  $\frac{1000}{2} \times 0.1071 = 53.55$  would represent the atomic heat of bromine.

According to the experiments of M. Regnault, however, the atomic heats of the simple bodies vary between the limits of 38 and 42, and bromine would thus form an exception to the law of Dulong and Petit, as its atomic heat is about one-fourth higher than that required by theory. This discrepancy is attributed by Dr. Andrews to the specific heat being necessarily determined in the liquid state, and he considers that bromine would agree with the law of Dulong and Petit, and its specific heat be about 0.08, if this could be ascertained with the solid substance.

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*On the determination of Nitrogen in analysis, by JOHN MITCHELL, Esq.*  
—Mr. Mitchell recommends a further modification of Will and Varantrapp's process, based upon that proposed by Peligot,\* for rendering the estima-

\* Comptes Rendus, March 29, 1847.

tion of nitrogen more expeditious. The latter consists in using a solution of sulphuric acid, of known strength, in the bulbous tube, in place of the muriatic acid of the original process, and in ascertaining, by means of a solution of lime in sugar, also of definite strength, what proportion of the acid has been saturated by the ammonia produced in the combustion with soda-lime. Mr. Mitchell objects to the use of lime dissolved in sugar, on account of the tendency which it has to undergo spontaneous decomposition, and also to form carbonate with the carbonic acid of the air, and become altered in strength; he substitutes, therefore, a weak solution of caustic soda (sp. gr. 1.018), and the quantity of this which is consumed in any experiment he prefers to weigh from a Schuster's alkalimeter, instead of measuring by a burette.

For neutralizing the acid with greater accuracy than can be obtained by the use of litmus, a decoction of logwood is recommended, a few drops of which impart a yellowish-brown colour to the acid liquid, and this is converted into a distinct blackish blue by the minutest possible excess of the alkaline solution. The accuracy of the process, as compared with that of Will and Varräntrapp, was verified by two experiments with Hyson tea.

The original process yielded	5.81	nitrogen
The modified process . . .	5.80	"

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### III. Analysis of Bichromate of Ammonia and some double salts of Chromic Acid. By MR. STEPHEN DARBY.

1. *Bichromate of Ammonia*.—This salt, as is well known, may readily be prepared by partially saturating a solution of chromic acid with ammonia, and crystallizing, to remove any adhering sulphate of ammonia. As no analysis of the salt has hitherto been published, it was of interest to determine whether the ammonia in combination with the acid was anhydrous or analogous to potash. The following are the results of my experiments.

It has already been shown by Hayer and Böttger, that this salt is decomposed on the application of heat, giving off water, whilst pure oxide of chromium remains, in appearance, bearing a great resemblance to tea. On heating it in a tube, the escape of free undecomposed ammonia is perceived, sufficient, in fact, to cause a loss of 2 per cent in the water when the substance is heated *per se*. The temperature at which it is decomposed I found to be 200° C. (392° F.). The following are the results of the analyses of pure bichromate of ammonia dried in the air:

I. 0·349 grm. gave 0·224 ox. chromium = 84·96 per cent chromic acid.

II. 0·208 gave 0·135 chromic oxide = 85·2 per cent chromic acid.

III. 0·736 grm. heated alone gave 0·154 water = 20·9 per cent.

IV. 0·555 grm. heated with chromate lead gave 0·128 grammes of water = 23·0 per cent.

At the end of each combustion the point of the tube was broken off, and the remaining vapour drawn into the chloride of calcium tube. Thus the following formula is deduced from my analysis :

	Calc. per cent.	Found.		
			I.	II.
1 at Ammonia, NH <sub>3</sub> . . .	17·0	14·4	13·14	14·4
2 „ Chromic acid, 2Cr O <sub>3</sub>	100·6	85·5	84·96	85·2
NH <sub>3</sub> 2Cr O <sub>3</sub> =	<u>117·6</u>	<u>99·9</u>	<u>98·10</u>	<u>99·6</u>

The three atoms of hydrogen being oxidised by half the oxygen of the acid, form 23 per cent of water; if oxide of ammonium composed the base of the salt (NH<sub>4</sub> O, 2Cr O<sub>3</sub>), the required per centage of water would be 28·6.

On the addition of caustic potash to the salt, ammoniacal vapours were instantly given off; it also yielded a precipitate with chloride of platinum, thus differing from anhydrous sulphate of ammonia.

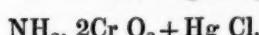
The neutral chromate of ammonia consists, according to Kopp, of NH<sub>4</sub> O, Cr O<sub>3</sub>, containing one atom of water; analysis yielded me 47·0 per cent of water, thus agreeing with the formula assigned it.

2. *Double salt of the Bichromate of Ammonia with Chloride of Mercury.*—On dissolving equivalent quantities of bichromate of ammonia and corrosive sublimate in water, deep-red crystals were obtained by evaporation, which gave on analysis the following results :

I. 0·728 grm. gave 0·224 oxide of chromium.

II. 0·680 grm. gave 0·212 oxide of chromium.

	Calc. per cent.	Found.		
			I.	II.
2 at. Chromic acid . . .	100·6	39·7	40·4	40·8
1 „ Ammonia . . . .	17·0			
1 „ Corrosive sublimate .	<u>135·4</u>			
		253·0	agreeing with the formula :	



3. *Double salt of Bichromate of Potash with Chloride of Mercury.*—On evaporating a solution containing equivalent quantities of bichromate of potash and chloride of mercury, the double salt

is obtained in beautiful red, pointed crystals, which are anhydrous, and have the formula KO, 2Cr O<sub>3</sub> + Hg Cl.

I. 1·699 grm. of the salt gave 0·722 sulphide of mercury and 0·448 oxide of chromium.

II. 0·181 grm. gave 0·109 chloride of silver, or :

	Calc. per cent.	Found.
1 equiv. Potash . . .	47·2	" "
2 equivs. Chromic acid . .	100·6	35·5
1 equiv. Chlorine . . .	35·4	12·5
1 " Mercury . . .	100·0	35·0
KO, 2Cr O <sub>3</sub> + Hg Cl =	283·2	

The excess of chlorine is accounted for, by a portion of the chromic acid being precipitated, which even hot nitric acid would not entirely dissolve.

This salt was previously described by Millon,\* who assigns it the same constitution.

4. *Double salt of Neutral Chromate of Potash with Chloride of Mercury.*—On mixing a solution of neutral chromate of potash with one of corrosive sublimate, a brick-red precipitate of basic chromate of oxide of mercury is formed, which has also been described by Millon.† My analysis agrees with the formula 3Hg O + Cr O<sub>3</sub>.

I. 0·285 grm. of the salt dried over sulphuric acid gave 0·030 oxide of chromium.

II. 0·521 grm. gave 0·054 oxide of chromium, or :

	Calc. per cent.	Found.
3 equiv. Oxide of mercury .	324	86·5
1 " Chromic acid . .	50·3	13·5
3Hg O, Cr O <sub>3</sub> =	374·3	100·0

On evaporating the solution filtered from the above precipitate, small crystals are formed, of a pale-red colour, which readily dissolve in water, yielding a yellow solution. The analysis of these yielded the following results :

I. 0·638 grm. gave 0·065 oxide of chromium and 0·157 sulphate of potash.

II. 0·342 grm. gave 0·205 sulphide of mercury and 0·077 sulphate of potash.

III. 0·370 grm. gave 0·038 oxide of chromium.

IV. 0·198 grm. gave 0·171 chloride of silver.

\* Berzelius, *Jahresbericht*, xxv. p. 293. † *Annales de Chim. et de Phys.* xviii. p. 333.

V. 0·274 grm. gave 0·236 chloride of silver.

	Calc. per cent.	Found.	I.	II.	III.
1 equiv. Potash . . .	47·2	12·6	13·3	12·1	
1 „ Chromic acid . .	50·3	13·4	13·3	13·4	13·4
2 equivs. Mercury . .	200·0	53·6	„	51·2	
2 „ Chlorine . .	70·8	20·4	21·3	21·1	
$\text{KO}_2\text{CrO}_3 + 2\text{HgCl} = 368\cdot3$		100·0			

The same salt may be directly prepared with equivalent quantities of chromate of potash and chloride of mercury, or with two of the latter and one of the former, to which just sufficient hydrochloric acid is added to dissolve the precipitate formed on mixing them; the salt which crystallizes has the same composition as the preceding one.

5. *Double salt of Neutral Chromate of Potash with Cyanide of Mercury.*—This salt has been previously described by Caillot and Podevin,\* and by Rammelsberg.† The former assign it the formula  $\text{KO}_2\text{CrO}_3 + 2\text{HgCy}$ , which is given by L. Gmelin ;‡ according to Rammelsberg, however, the formula is  $2\text{KO}_2\text{CrO}_3 + 3\text{HgCy}$ ; and it is with the latter that the results of my analysis agree.

The salt is formed by evaporating together solutions of equivalent parts of chromate of potash and cyanide of mercury; it yields fine laminated crystals of a clear yellow colour, readily soluble in water.

I. 0·383 grm. gave 0·50 oxide of chromium.

II. 0·255 grm. gave 0·159 sulphide of mercury.

III. 0·305 grm. gave 0·108 sulphide of mercury and 0·041 oxide of chromium.

IV. 1·363 grm. gave 0·805 sulphide of mercury, 0·188 oxide of chromium, 0·415 sulphate of potash.

	Calc. per cent.		By experiment.		
			I.	II.	III.
2 equivs. Potash . . .	94·4	16·7	„	„	16·40
2 „ Chromic acid . .	100·6	17·5	17·07	17·60	18·09
3 „ Mercury . .	300·0	52·2	52·47	50·80	50·80
3 „ Cyanogen . .	78·0	„	„	„	„
$2\text{KO}_2\text{CrO}_3 + 3\text{HgCy} = 573\cdot0$					

Rammelsberg found in 100 parts 17·28 potash, 17·60 chromic acid, and 51·14 mercury, numbers, nearly in accordance with the above analysis.

\* *Compt. Rend.* xxiii. p. 766.

† *Pogg. Annalen* xlvi. p. 131.

‡ L. Gmelin, *Handbuch*, iv. p.

6. *Double salt of Chromate of Silver and Cyanide of Mercury.*—On adding nitrate of silver to a solution of the salt just described, as long as a precipitate is formed, and then heating the mixture almost to the boiling point, with just as much nitric acid as is required to dissolve the whole, beautiful red, needle-shaped crystals are formed on cooling, which are scarcely soluble in cold, but more readily so in hot water. They contain neither nitric acid nor potash, are decomposed on heating with strong nitric acid, and explode at a high temperature. Analysis assigns them the formula  $\text{Ag O, } 2\text{Cr O}_3 + 2\text{Hg Cy}$ .

I. 0·704 grm. gave 0·219 chloride of silver and 0·116 oxide of chromium.

II. 0·682 grm. gave 0·215 chloride of silver and 0·112 chromic oxide.

	Calc. per cent.	Found.	
		I.	II.
1 equiv. Oxide of silver . . .	116·0	24·7	25·1
2 equivs. Chromic acid . . .	100·6	21·3	21·6
2 „ Mercury . . .	200·0		
2 „ Cyanogen . . .	52·0		
$\text{Ag O, } 2\text{Cr O}_3 + 2\text{Hg Cy}$	=468·6		

7. *Neutral Subchromate of Mercury.*—On mixing a solution of subnitrate of mercury with neutral chromate of potash, a precipitate, as is well known, of subchromate of mercury is formed, which according to the analysis of Godon and L. Gmelin,\* consists of 4 equivalents of suboxide of mercury and 3 equivalents of chromic acid. On boiling this precipitate with dilute nitric acid, it is converted into a crystalline powder, or when corrosive sublimate or nitrate of mercury is added to a solution of the yellow salt ( $2\text{KO, Cr O}_3 + 3\text{Hg Cy}$ ), with a small quantity of nitric acid, as much as will exactly dissolve the precipitate, and this solution is heated almost to the boiling point, the chromate of mercury is precipitated on cooling, as a sub-salt, in a fine red crystalline powder. The whole of the mercury in this salt is precipitated by hydrochloric acid from the solution in nitric acid. Ammonia and potash both give black precipitates with this salt. The analyses were as follows :

I. 0·246 grm. of the salt prepared directly gave 0·036 oxide of chromium.

II. 0·383 grm. of the salt prepared from the double salt gave 0·057 oxide of chromium.

\* *Handbuch*, iii. p. 572.

III. 0·453 grm. of the salt prepared from the double salt gave 0·067 oxide of chromium.

		Calc. per cent.	Found.	I.	II.	III.
1 equiv. Chromic acid . . .	50·3	19·14	19·2	19·5	19·1	
1   , Subox. of mercury	208·0					
$Hg_2 O + Cr O_3 = 258·3$						

Dec. 6, 1847.

The President in the chair.

M. Dumas was elected a foreign member, and S. E. Churchill, Esq., Chemist to the Royal Agricultural Society of Jamaica, a non-resident member of the Society.

The following communications were read :

*On the preparation of Creatine, and on the proportions of that substance contained in different kinds of flesh and fish, by WILLIAM GREGORY, M.D., F.R.S.E.*—The process followed by the author in the preparation of creatine from the flesh of birds and quadrupeds, is that described in Baron Liebig's work, "On the Chemistry of Food," translated by Dr. Gregory; but as a cheap source of this sparingly disseminated substance, the flesh of cod or skate is recommended, which, although yielding a two or three times lesser amount of creatine, is nevertheless five times more economical, and the facility afforded by it in the preparation of the substance is greater. The only fish from which creatine was obtained by Liebig, was the pike; and he found a difficulty in submitting the hacked flesh to pressure, which obliged him to obtain the latter portions of the fluid by displacement with water on a strainer; this is not found to be the case with cod or haddock, from which the fluid portion can be more completely expressed than from fowl or butcher-meat; less water is consequently necessary in the operation, and more of the flesh can be employed at once. The chopped fish is mixed with an equal weight of water, or at most with 4 parts of water to 3 of fish, and a second extraction is found unnecessary, for the fish may be pressed nearly quite dry. When, after coagulating the albumen, the barytes is added, the liquid from fish is apt to remain turbid, part of the precipitate not subsiding, and passing at first even through the filter. This precludes the possibility of ascertaining when the proper amount of barytes has been added, but the use of turmeric paper (which in all cases is preferred to litmus by Dr. Gregory), immediately shows when a sufficiency of barytes has been employed.

As was the case in Liebig's experiments with pike, so with cod, skate, and haddock, the liquid when finally concentrated to a certain point, gelatinizes on cooling, and in this jelly the crystals of creatine are formed.

When the evaporation has not been carried too far, the addition of cold water readily liquifies the jelly and causes the crystals to collect at the bottom of the vessel, the liquid may then be decanted off with facility. The crystals thus obtained are in a state of great purity, and hardly require re-crystallization. In the haddock alone, the creatine was mixed with a good deal of another substance, soluble in water and alcohol, the nature of which the author has not yet further examined.

The following are the quantities of creatine obtained by Liebig and by the author from different sources.

100 parts of the flesh of	Liebig.	Gregory.
Fowl yielded of creatine . . .	3·2 { No. 1. " 2. }	3·21 2·90
Ox " . . . . .	0·697	
Horse " . . . . .	0·72	
Ox-heart " . . . . .	{ No. 1. " 2. }	1·375 1·418
Pigeon " . . . . .		0·825
Skate " . . . . .	{ No. 1. " 2. }	0·607 0·050?
Cod " . . . . .	{ " 1. " 2. }	0·935 1·741
Goose " . . . . .		0·895
Haddock " . . . . .		0·614
Brill " . . . . .		0·7
Herring " . . . . .		1·324

The quantities of creatine obtained from cod at different times, stated in the table as Nos. 1 and 2, clearly show that the proportion of this substance varies in the same kind of flesh, as the same process was followed in both cases without the occurrence of any apparent differences during the operation. The two results obtained from skate also prove this, and in the second experiment, No. 2, noticed with a point of interrogation in the table, no crystals were deposited, even when the liquid had been evaporated to the consistence of a thick jelly, but on boiling the jelly with alcohol, a small desposition of crystals ensued, which when re-crystallized from water, appeared as fine slender prisms, evidently quite distinct from creatine, as they were not altered by a temperature of 212° F. It appeared as if the creatine, in this case, were replaced by one or more different compounds, although on reboiling the jelly with alcohol, a very small crop of crystals of creatine was obtained.

In the experiment with haddock, the addition of barytes caused a distinct disengagement of ammonia, and the creatine obtained was less pure than in any other instance, being accompanied by another substance, the nature of which was not ascertained.

In neither of the two last kinds of fish named in the table, did the concentrated liquid gelatinize, as in pike, skate, and cod. It rather

assumed the thick, syrupy consistence of the liquid from fowl or beef. In the case of the brill, as in that of the haddock, ammonia was given off on the addition of the barytes; and during the evaporation, the liquid acquired an offensive smell, at first somewhat resembling that of putrescence, but afterwards becoming exactly similar to the fetor of the evacuations in dysentery and other diseases of the mucous membrane of the intestines. It is important to observe that in the decomposition thus indicated, the creatine did not disappear, and that the liquid continued neutral. Liebig has found that creatine disappears in the putrefaction of urine, probably in consequence of the presence of free ammonia.

The author did not succeed in obtaining creatinine from the syrupy liquid which deposited the first crop of crystals of creatine, but from the mother liquids left on the recrystallization of creatine perfectly neutral chloride of zinc produced Pettenkofer's compound, which is a mixture of creatine with chloride of zinc and creatinine. Dr. Gregory is, therefore, inclined to think that the creatinine is formed from the creatine during the process, and is not, as Liebig supposes, a constant ingredient in the juice of flesh.

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*IV. On the Latent Heat of Vapours.* By THOMAS ANDREWS, M.D.  
M.R.I.A.

SINCE the period when Black first explained his celebrated doctrine of Latent Heat, and showed the general method of measuring the quantities of heat evolved or abstracted during the changes of bodies from one physical state to another, the subject has attracted the attention of several distinguished inquirers both in this country and on the continent. It would be foreign to my present purpose to enter into a detailed account of their methods or results, which is indeed the less necessary, as a very complete history of the subject, accompanied by critical remarks, will be found in an able Memoir, published a few years ago in Poggendorff's *Annalen*,\* by Dr. Brix, of Berlin. More recently, two important communications on this subject have been made to the Academy of Sciences of Paris; one by M. Regnault, on the Latent Heat of Steam when generated under different pressures; the other by MM. Favre and Silbermann, on the Latent Heat of the Vapours of several Organic Liquids.

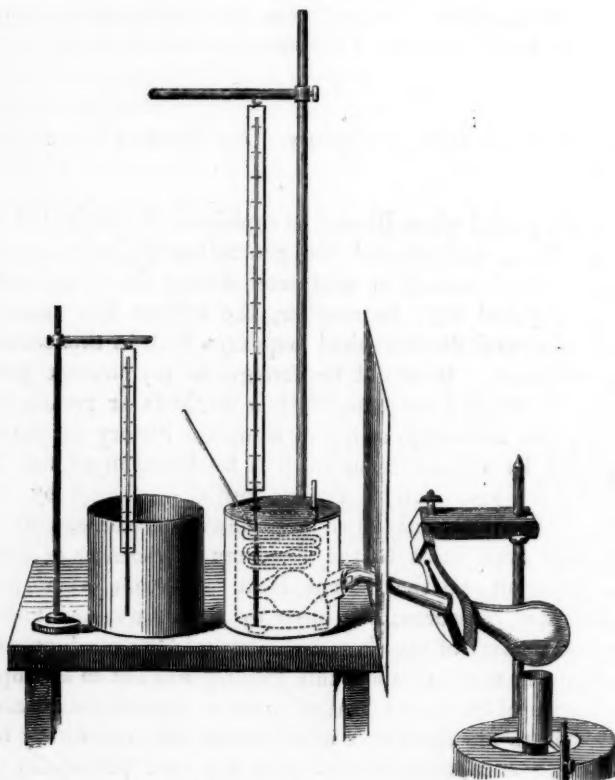
My object in entering upon this inquiry was not to attempt a new determination of the latent heat of aqueous vapour, but to extend the investigation to the vapours of other bodies differing widely from one another in chemical composition, with the view principally of ascertaining whether any fixed relation exists between the latent heat and

\* Bd. LV. s. 341.

the other physical properties of vapours. In this inquiry, I have been preceded by Ure, Despretz, Brix, and Fabre and Silbermann. Their results are, for the most part, remarkable for accuracy, but, with the exception of those of the last-named experimentalists, extend only to a very small number of substances. Even their experiments, however, only embrace compounds of oxygen, hydrogen, and carbon. By employing a very delicate glass apparatus, I have been enabled to supply, in some measure, this deficiency, and to extend the inquiry to one simple substance, and a small number of inorganic compounds.

The apparatus employed in these experiments is represented in Fig. 1. The fluid to be converted into vapour is placed in a

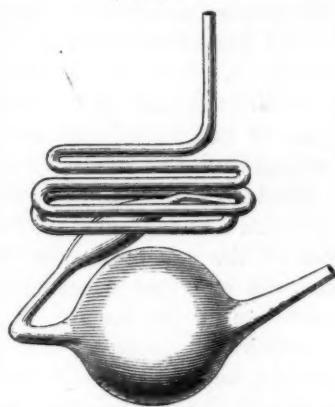
FIG. 1.



small glass flask, the neck of which has a very short bend, as shown in the figure. Into this the end of the receiver is inserted, by means

of a small cork. The form of the receiver is shown in Fig 2. It

FIG. 2.



consists of a very thin bulb of German glass, terminating in a spiral tube of the same material. The glass receiver is fixed by a cork in a light copper vessel (Fig. 3), from which it can be easily removed at the end of the experiment. The copper vessel, which is open above, is filled with water, cooled from  $1^{\circ}$  to  $2^{\circ}$  C. ( $1^{\circ}8 - 3^{\circ}6$  F.) below the temperature of the air. The whole is surrounded by an outer vessel of tin-plate,

FIG. 3.



fitted with a moveable lid in which are three openings, one for the thermometer, another for the extremity of the spiral tube of the receiver, and a third for the stirrer, which is formed of a very light and hollow glass tube. An additional screen, as shown in the figure, is interposed between the lamp by which the liquid is heated, and the rest of the apparatus.

The thermometer employed is very delicate, and the greatest pains were taken to insure its accuracy. The diameter of the reservoir is not greater than that of a thin thermometer tube, and it occupies the entire depth of the calorimeter. It is attached to an arbitrary metallic scale, divided into fiftieth parts of an inch. The errors of calibre were determined by two distinct measurements of columns of mercury of different lengths; the freezing point was ascertained by direct observation, and another point situated near  $25^{\circ}$  C. ( $77^{\circ}$  F.), by comparison with an accurate thermometer, constructed by Greiner. It was easy from these data to prepare a table, showing the degree corresponding to each arbitrary division of the scale, and also the multiplier, required to reduce an increment observed at any part of the scale, into true degrees. Two independent tables were constructed from the separate measurements, and they were found to differ nowhere more than  $0^{\circ}01$  C. ( $0^{\circ}018$  F.). Within the ordinary limits of atmospheric temperature, the difference of the expansion of a metallic or glass scale for increments of a few degrees is so slight, that it may be neglected. The correction for the mercury in the stem of the thermometer is more important. The multipliers for the divisions of the arbitrary scale were corrected accordingly.

The increments of temperature, as obtained by observation, were carefully corrected for the cooling and heating influence of the surrounding air. From one to two minutes were occupied in raising the liquid to the point of ebullition ; and during this period, the thermometer remained nearly at the same point. While the ebullition continued, the thermometer rose very steadily and uniformly, but it did not attain the maximum point till about two minutes after the ebullition had ceased. For the heat gained and lost during these periods, a correction, deduced from direct experiments with the calorimeter alone, was applied. The agitation was continued for five minutes after the thermometer had reached the maximum, and the difference between the loss of heat observed, and that indicated by calculation, was added as a further correction to the result. This last is frequently omitted in inquiries such as the present, but it generally amounts to an appreciable quantity, and in accurate experiment ought never to be neglected. To prevent the mercurial column from becoming heated by the person of the observer, the divisions were read through a powerful magnifier, which was fixed on a moveable support.

In addition to the causes of error already referred to, others exist of not less importance, but the effect of which it is much more difficult to estimate. If the liquid be boiled too slowly, a portion of the vapour will be condensed in the tube of the receiver just before it enters the calorimeter, and a considerable loss of heat will occur. On the other hand, if the ebullition is carried on very rapidly, an undue pressure will be produced in the interior of the retort, the temperature of the vapour will be raised above the ordinary boiling point, and too large an increment finally obtained. A portion of uncondensed but partially cooled vapour will also escape, particularly at the commencement of the operation, before the air has been expelled. On this part of the subject, an elaborate mathematical investigation will be found in the memoir of Dr. Brix, to which reference has already been made ; but it may be doubted whether the experimental data are yet sufficiently precise to admit of the useful application of formulas derived from the higher branches of analysis. To ascertain, as far as possible, the limits of error to which the apparatus now described is liable, I made two series of experiments with water and alcohol ; in the first, the ebullition occupied from one and a half to two minutes ; in the second, from three and a half to five minutes. In order to complete the operation in the shortest period, the liquid was made to boil very violently, and there can be no doubt that the vapour was generated under a higher pressure than that of the

atmosphere. In the other case, the ebullition proceeded at a gentle rate, and all the causes of error tended to render the results too low. The mean number given by the experiments of the first series for the latent heat of water, was  $541^{\circ}4$  C. ( $1038^{\circ}5$  F.); and by those of the second,  $532^{\circ}7$  C. ( $1023^{\circ}$  F.). The mean of the whole was  $535^{\circ}9$  C. ( $1030^{\circ}75$  F.). This latter number agrees very closely with the mean of the results obtained by Despretz, Dulong, and Brix, and is almost identical with that recently arrived at by M. Regnault.\* From these observations, it follows that when the operation was purposely so performed as to exaggerate to the utmost the errors occasioned by the apparatus, the result does not diverge more than  $\frac{1}{100}$ th part from the true number. The experiments with alcohol lead to the same conclusion; the mean of the series, in which the ebullition occupied the shortest period, being  $205^{\circ}0$  C. ( $401^{\circ}$  F.), and of that in which it occupied the longest period  $202^{\circ}4$  C. ( $396^{\circ}3$  F.); so that the difference here was even less than in the experiments with water. In determining the latent heat of other bodies, the fluid was made to boil as fast as was possible, without producing increased pressure on the interior of the apparatus. In the case of a few liquids, it was found difficult to complete the vaporization in the ordinary time, and hence the results expressing their latent heats are probably a little below the true numbers. This remark applies particularly to the iodic and oxalic ethers, and to the iodide and acetate of methyl.

The weight of the condensed vapour was ascertained by weighing the glass receiver (Fig. 2) at the end of the experiment, and deducting the weight of the same when empty.

The boiling points of all the liquids operated on were determined with great care. This is often attended with considerable difficulty, and even distinguished chemists have committed serious mistakes in examining the boiling points of volatile fluids. The numbers given in this paper were obtained by heating the liquid with a very small spirit flame in a glass retort, the thermometer being immersed in the vapour, at a short distance above the surface of the liquid. A quantity of mercury was placed in the retort, except in the case of liquids which attacked that metal. The results given by observation were corrected for the portion of mercury in the stem of the thermometer, which was not heated in the vapour, and also for the variations of the barometer. In making the latter correction, it was assumed, as a sufficient approximation, that the boiling points of other liquids were raised or depressed to the same extent as that of water by the same changes in the height of the barometer.

\* Their numbers are, 531, Despretz; 543, Dulong; 540, Brix; 536·4, Regnault.

The specific heats of several of the liquids were determined by direct experiment. The liquid raised to the boiling point was quickly introduced into a thin glass tube immersed in water, and the gain of heat of the latter observed. The results in general agreed very closely with those of Regnault. In other cases, I have employed the numbers given by the same accurate observer, which were in general determined by observing their rates of cooling. A slight error may thus be produced, in consequence of the specific heat of the liquid not being the same at different temperatures, but for the liquids actually employed, this difference is probably unimportant.

Finally, every precaution was taken to operate on perfectly pure chemical substances. This is of much more importance in such inquiries as the present, than even in analytical investigations, from the great differences in the specific heats of the same weight of different liquids. Thus, the presence of only  $\frac{1}{100}$ th part by weight of aqueous vapour would induce an error of  $\frac{1}{17}$ th part in the determination of the latent heat of the vapour of ether.

The weight and thermal value, in terms of water, of the different parts of the apparatus were as follows :

Copper vessel	49.5 grms.	$\times 0.095$	4.7 grms.
Glass receiver	13.7	$\times 0.183$	2.5
Thermometer, stirrer, and cork	. . .	. . .	0.5
Thermal equivalent of apparatus	. . .	. . .	<u>7.7</u> grms.

In stating the results, I have used the following abbreviations :

Bar. : the height of the barometer reduced to 0.

Air : the temperature of the air in centigrade degrees.

Ex. : the excess of the final temperature of the water in the calorimeter above the air.

Inc. : the increment of temperature, as obtained by observation.

T : the time of ebullition.

T' : the time from the observation of the initial temperature till the thermometer attained its maximum.

V : the weight of condensed vapour.

W : the weight of the water in the calorimeter, exclusive of the thermal value of the vessels.

L.H. : the latent heat corrected.

*Water.*—Specific heat 1.00. Boiling point, under a pressure of 29.92 inches, at 100° C. (212° F.).

#### FIRST SERIES.

	I.	II.	III.
Bar.	29.52 in.	30.43	30.14

I.	II.	III.	IV.
Air.	6°50	8°60	9°90
Ex.	2°69	2°00	1°97
Inc.	4°083	3°411	3°761
T	1°20"	1°35"	1°50"
T'	3°45"	3°30"	5°0
V	1.860 gm.	1.573 gm.	1.766 gm.
W	2792.2 grms.	2823 grms.	286.2 grms.
L.H.	542.9	543.4	537.9

Mean latent heat, 541.4.

#### SECOND SERIES.

I.	II.	III.	IV.	V.
Bar.	29.70 in.	30.10 in.	30.10 in.	30.09 in.
Air.	11°30	10°10	10°44	9°55
Ex.	2°08	1°87	2°20	1°83
Inc.	3°772	3°833	4°078	4°039
T.	4°35"	4°0"	3°15"	3°35"
T'.	7°10"	6°15"	5°45"	5°40"
V.	1.780 gm.	1.829 gm.	1.980 gm.	1.921 gm.
W.	285.1 grms.	287.8 grms.	293.8 grms.	287.7
L.H.	536.8	531.9	532.2	531.6

Mean latent heat, 532.7.

Mean of whole series, 535.9.

*Alcohol.*—The alcohol was purified by repeated distillations from lime in a vapour-bath. It was deprived of essential oil by charcoal. It boiled at 78°3 C. (173°0 F.) under a pressure of 30.3 in.; and hence its true boiling point, under a pressure of 29.9 in., is 77°9 C. (172°3 F.). The mean of three experiments gave for its specific heat, 0.617.

#### FIRST SERIES.

I.	II.	III.
Bar.	29.75 in.	29.75 in.
Air.	14°20	14°95
Ex.	1°50	2°00
Inc.	3°467	3°367
T.	1°55"	2°0"
T'.	4°25"	4°40"
V.	4.202 gms.	4.167 gms.
W.	286.0 "	289.4 "
L.H.	204.8	203.9

Mean latent heat, 205.0.

## SECOND SERIES.

I.	II.	III.	IV.	V.
Bar. 29.90 in.	29.90 in.	29.91	29.91	29.90
Air. 11°.10	11°.10	10°.80	10°.70	10°.60
Ex. 2°.38	1°.90	1°.56	1°.92	1°.72
Inc. 4°.417	3°.833	3°.533	3°.878	3°.567
T. 4'25"	4'35"	3'40"	3'50"	4'25"
T'. 6'40"	6'45"	4'55"	5'25"	6'0"
V. 5.381 gms.	4.785 gms.	4.402 gms.	4.830 gms.	4.430 gms.
W. 286.3 "	292.2 "	293.0 "	291.4 "	289.5
L.H. 201.7	201.4	201.5	199.7	199.7

Mean latent heat, 200.8.

Mean of whole series, 202.4.

*Bromine*.—Pure bromine, according to my experiments, boils under a pressure of 29.9 in. at 58° C. (136°.6 F.), and its specific heat is 0.107.\*

	I.	II.	III.	IV.
Bar.	30.01 in.	29.99 in.	29.70 in.	29.70 in.
Air.	6°.30	6°.50	5°.70	5°.70
Ex.	1°.33	1°.28	1°.33	1°.55
Inc.	2°.659	2°.708	2°.568	2°.975
T.	2'45"	3'30"	3'55"	2'55"
T'.	5'30"	6'30"	6'45"	6°.15"
V.	14.983 gms.	15.291 gms.	14.638 gms.	16.910 gms.
W.	279.8 "	279.2 "	279.3 "	279.2 "
L.H.	45.95	45.62	45.28	45.56

Mean latent heat, 45.60.

*Protochloride of Phosphorus*.—The protochloride was prepared by the action of dry chlorine gas on phosphorus. It was afterwards digested for several days with an excess of phosphorus, and purified by repeated distillations. It was perfectly limpid and colourless. and under a pressure of 30.20 in., it boiled at 78°.5 C. (173°.4 F.). I have taken Regnault's number (0.209) for its specific heat.

	I.	II.	III.
Bar.	29.54 in.	29.29 in.	29.49 in.
Air.	4°.90	7°.16	10°.33
Ex.	1°.67	2°.11	2°.21
Inc.	2°.556	3°.017	3.733
T.	2'30"	2'35"	3'5"

\* See present number, p. 19.

	I.	II.	III.
T'	5'30"	5'30"	6'0"
V.	11.245 gms.	13.122 gms.	16.531 gms.
W.	280.0	276.5	278.0
L.H.	51.11	51.77	51.39

Mean latent heat, 51.42.

*Bichloride of Tin.*—This compound was prepared by the action of dry chlorine on tin, and after being deprived of the excess of chlorine by digestion with tin filings, was purified by repeated distillations. It boiled at 112°.5 C. (233°.9 F.) under a pressure of 29.60 in. Its specific heat was assumed to be 0.148.

	I.	II.	III.
Bar.	30.12 in.	30.12 in.	30.17 in.
Air.	6°.10	6°.10	6°.40
Ex.	1°.64	1°.55	1°.28
Inc.	2°.578	3°.006	2°.700
T.	2',15"	2',0"	2',45"
T'	6',30"	5',30"	6',0"
V.	16.232 gms.	18.555 gms.	16.924 gms.
W.	278.8	278.8	278.8
L.H.	30.37	31.02	30.21

Mean latent heat, 30.53.

*Sulphuret of Carbon.*—This liquid was digested with chloride of calcium, and distilled. It boiled, under a pressure of 30.30 in., at 46°.2 (115° F.) Specific heat assumed to be 0.319 (Regnault).

	I.	II.	III.
Bar.	29.92 in.	30.27 in.	30.27 in.
Air.	9°.10	9°.05	8°.94
Ex.	2°.83	3°.00	3°.44
Inc.	4°.422	4°.467	4°.761
T.	3',30"	3',0"	3',45"
T'	5',55"	5',30"	6',25"
V.	13.465 gms.	13.618 gms.	14.548 gms.
W.	276.7	276.8	277.1
L.H.	86.72	86.56	86.72

Mean latent heat, 86.67

*Sulphuric Ether.*—This ether was purified in the usual manner. It boiled under a pressure of 29.61 in., at 34°.9 C. (94°.73 F.) Specific heat, 0.517.

	I.	II.	III.
Bar.	30·18 in.	30·16 in.	30·16 in.
Air.	2 <sup>0</sup> .30	8 <sup>0</sup> .10	8 <sup>0</sup> .10
Ex.	1 <sup>0</sup> .78	1 <sup>0</sup> .94	2 <sup>0</sup> .11
Inc.	3 <sup>0</sup> .783	3 <sup>0</sup> .572	3 <sup>0</sup> .806
T.	4',15"	3',50"	3',50"
T'.	6',25"	6',10"	6',20"
V.	10·477 gms.	9·812 gms.	10·473 gms.
W.	277·0 ,	277·1 ,	276·5 ,
L.H.	89·89	90·94	90·50

Mean latent heat, 90·45.

*Iodic Ether.*—This ether was prepared by taking 14 gms. phosphorus and 70 gms. alcohol, sp. gr. 0·816, and adding in small portions 46 gms. iodine, waiting between each addition of iodine till the liquid became clear. It was then distilled at a gentle heat, washed with water, and allowed to digest for forty-eight hours with an excess of chloride of calcium. It was again distilled at a temperature of from 70° to 75°. (158°—167° F.) The purification was finally completed by another digestion with chloride of calcium, and distillation. Its boiling point was found to be 71°·3, (160°·36 F.), under a pressure of 29·9 in.

	I.	II.	III.	IV.
Bar.	29·53 in.	29·39 in.	29·40 in.	29·40 in.
Air.	7 <sup>0</sup> .70	7 <sup>0</sup> .05	7 <sup>0</sup> .90	8 <sup>0</sup> .05
Ex.	2 <sup>0</sup> .39	1 <sup>0</sup> .72	2 <sup>0</sup> .28	2 <sup>0</sup> .44
Inc.	3 <sup>0</sup> .939	3 <sup>0</sup> .294	3 <sup>0</sup> .717	4 <sup>0</sup> .256
T.	5',35"	6',5"	6',0"	6',0"
T'.	8',20"	9',20"	8',55"	9',30"
V.	20·974 gms.	17·504 gms.	19·590 gms.	22·170 gms.
W.	289·6 ,	292·1 ,	285·2 ,	283·7
L.H.	46·94	46·78	46·83	46·94

Mean latent heat, 46·87.

*Oxalic Ether.*—The oxalic employed in the following experiments, boiled at 184·4 (396° F.), under a pressure of 30·7 in. Specific heat, 0·457.

	I.	II.	III.
Bar.	30·66 in.	30·60 in.	30·60 in.
Air.	6 <sup>0</sup> .20	7 <sup>0</sup> .50	7 <sup>0</sup> .60
Ex.	2 <sup>0</sup> .89	1 <sup>0</sup> .50	2 <sup>0</sup> .89
Inc.	4 <sup>0</sup> .744	3 <sup>0</sup> .772	4 <sup>0</sup> .333
T.	3',10"	5',35"	3',15"

	I.	II.	III.
T.	7'25"	9'50"	8'30"
V.	9.177 gms.	7.335 gms.	8.461 gms.
W.	284.3 "	288.5 "	284.8 "
L.H.	73.33	72.61	72.22

Mean latent heat, 72.72.

*Acetic Ether.*—This ether, carefully purified, was found to boil at 74°.6 (166°.36 F.), under a pressure of 30 in. Its specific heat in two trials was found to be 0.471 and 0.477; mean, 0.474.

	I.	II.	III.	IV.
Bar.	29.92 in.	29.90 in.	29.90 in.	29.89 in.
Air.	10°.20	10°.50	10°.90	11°.10
Ex.	2°.33	1°.94	1°.56	1°.78
Inc.	4°.500	4°.012	3°.967	3°.711
T.	5'55"	3'50"	3'10"	3'35"
T'	8'35"	6'45"	5'45"	6'30"
V.	10.804 gms.	9.524 gms.	9.468 gms.	8.761 gms.
W.	283.0 ",	283.7 ",	281.3 ",	279.6 "
L.H.	92.22	93.72	92.00	92.78

Mean latent heat, 92.68.

*Formic Ether.*—The easiest method of procuring formic acid for the preparation of this ether, is by distilling rapidly hydrated oxalic acid. On neutralizing the acid liquid which passes over with carbonate of soda, the greater part of the oxalic acid precipitates in the form of oxalate of soda, and by evaporation, the formiate of soda, mixed with a little oxalate, is obtained. This may be etherified without further purification, as the formic ether is easily and completely separated from the oxalic by distillation. Formic ether thus obtained, probably furnishes the easiest means of procuring formic acid and its salts in a state of purity. Formic ether boils under a pressure of 30 in. at 54°.3 (129°.9 F.). In three experiments its specific heat was found to be 0.485, 0.487, and 0.490; mean, 0.485.

	I.	II.	III.	IV.
Bar.	29.83 in.	29.57 in.	29.57 in.	29.57 in.
Air.	11°.05	9°.20	9°.67	9°.55
Ex.	1°.94	2°.00	1°.78	2°.28
Inc.	4°.006	3°.572	3°.439	4°.061
T.	2'45"	3'50"	3'55"	1'40"
T'	5'30"	6'20"	6'25"	4'10"
V.	9.323 gms.	8.508 gms.	8.092 gms.	9.379 gms.

	I.	II.	III.	IV.
W.	281·9 gms.	288·4 gms.	283·6 gms.	282·6 gms.
L.H.	105·3	105·0	104·2	106·7
Mean latent heat,	105·3.			

*Methylic Alcohol.*—The pyroxylic spirit of commerce was rectified several times over a water-bath from an excess of lime, the first and last portions being rejected. It was afterwards combined with chloride of calcium, and purified according to the method of Kane. It boiled at  $65^{\circ}8$  ( $150^{\circ}72$  F.), under a pressure of 30·2 in. In two experiments the numbers obtained for its specific heat were 0·611 and 0·615; mean, 0·613.

	I.	II.	III.
Bar.	29·72 in.	29·72 in.	29·71 in.
Air.	11°·10	11°·90	12°·20
Ex.	2°·50	1°·61	2°·61
Inc.	4°·089	4°·539	4°·800
T.	4'·5"	3'·15"	2'·35"
T'.	6'·35"	5'·50"	4'·55"
V.	4·039 gms.	4·451 gms.	4·743 gms.
W.	281·5 "	281·3 "	282·4 "
L.H.	264·0	262·4	264·6

Mean latent heat, 263·7.

*Iodide of Methyl.*—This compound was prepared by taking 50 gms. of purified wood-spirit and 10 gms. of phosphorus, and adding iodine in small quantities as long as it was dissolved. The quantity of iodine taken up by the liquid was about 69 grammes. The liquid was then distilled at a temperature varying from  $70^{\circ}$  to  $90^{\circ}$  ( $158^{\circ}$  —  $196^{\circ}$  F.) the distillate washed with ice-cold water, and added to a large excess of chloride of calcium with which it was allowed to digest for three days. It was afterwards rectified three times from chloride of calcium. It boiled at  $42^{\circ}2$  ( $108^{\circ}$  F.) under a pressure of 29·6 in. Specific heat assumed to be 0·158.

	I.	II.	III.	IV.
Bar.	29·71 in.	29·70 in.	29·81 in.	29·81 in.
Air.	9°·50	9°·45	8°·80	9°·20
Ex.	2°·06	2°·33	1°·56	1°·83
Inc.	3°·689	3°·883	3°·417	3°·761
T.	5'·15"	4'·50"	4'·50"	5'·55"
T'.	7'·40"	7'·20"	7'·25"	8'·30"
V.	21·465 gms.	22·446 gms.	20·011 gms.	21·460 gms.

	I.	II.	III.	IV.
W.	288·0 gms.	286·9 gms.	291·0 gms.	282·0 gms.
L.H.	46·06	46·39	46·00	45·83

Mean latent heat, 46·07.

*Acetate of Methyl.*—The impure acetate of methyl, obtained by distilling a mixture of purified wood-spirit, acetate of soda, and sulphuric acid, was digested with milk of lime, and chloride of calcium afterwards added in excess. After allowing the mixture to stand for twenty-four hours, the ether was decanted and digested for several days with chloride of calcium, and finally distilled in a water-bath, whose temperature never exceeded 65° (149° F.). It boiled, under a pressure of 30 in., at 55° (131° F.). Specific heat assumed to be 0·47.

	I.	II.	III.
Bar.	29·77 in.	29·78 in.	29·78 in.
Air.	10°00	10°10	10°60
Ex.	1°44	2°06	1°94
Inc.	3°806	3°633	3°578
T.	4'35"	4'40"	4'35"
T'	7'35"	8'5"	7'25"
V.	8·485 gms.	8·158 gms.	8·040 gms.
W.	283·8 "	284·2 "	284·1 "
L.H.	110·0	110·3	110·2

Mean latent heat, 110·2.

*Formiate of Methyl.*—It was prepared and purified by a process analogous to that last described. It boiled at 32°·9 (91°·2 F.) under a pressure of 29·6 in. Specific heat assumed to be 0·47.

	I.	II.	III.	IV.
Bar.	30·07 in.	30·07 in.	30·06 in.	30·06 in.
Air.	12°70	13°05	13°00	13°30
Ex.	1°17	1°28	0°94	1°40
Inc.	2°289	2°272	2°417	2°739
T.	3'45" *	3'10"	3'15"	3'20"
T'	6'5"	5'15"	5'25"	5'30"
V.	5·380 gms.	4·090 gms.	5·736 gms.	6·272 gms.
W.	289·0 "	291·4 "	294·5 "	282·7 "
L.H.	116·7	116·7	117·7	117·3

Mean latent heat, 117·1.

I have collected the foregoing results in the following table. The first column contains the latent heat for 1 gramme of each vapour;

the second for 1 liter, taken at the temperature of the point of ebullition of the vapour, and under the mean barometric pressure at which the experiments were performed.

	For 1 grammme.	For 1 liter.
Bromine . . . .	45·60	269·6
Protóchloride of phosphorus	51·42	244·4
Sulphuret of carbon . .	86·67	254·9
Bichloride of tin . . .	30·53	253·5
Water . . . .	535·90	318·3
Sulphuric ether . . .	90·45	268·2
Alcohol . . . .	202·40	324·2
Methylic alcohol . . .	263·70	303·5
Iodic ether . . . .	46·87	254·7
Iodide of methyl . . .	46·07	252·8
Acetic ether . . . .	92·68	287·9
Acetate of methyl . . .	110·20	303·6
Formic ether . . . .	105·30	290·3
Formiate of methyl . . .	117·10	282·8
Oxalic ether . . . .	72·72	291·4

It is obvious, from a cursory inspection of this table, that there exists some general relation between the volume of the vapour and its latent heat, but many other elements would require to be taken into consideration, before the precise nature of this relation can be determined. It has, indeed, been concluded, from a comparison I believe of the latent heats of water and alcohol, that the latent heat of equal volumes of different vapours is the same; but the experimental results now obtained do not support so very simple and general a relation. It is not improbable, however, that under certain physical conditions, the proposition may be correct, but until these are realized, and the result established by direct experiment, we cannot be justified in drawing so general a conclusion. It may be well to remark, that in the above table, the latent heats of equal volumes of each vapour taken at the respective boiling points of the fluids are compared; but in order to make the comparison more perfect, it would have been necessary to have examined equal volumes of the vapours taken at the same temperature. This could not, it is obvious, have been done, without operating under very different pressures, and thus introducing another source of complication into the results. Another circumstance, to which I may also refer, as connected with this subject, is the uncertainty that prevails as to the molecular constitution of some vapours near the temperatures at

which they condense. The recent experiments of Cahours leave, it is true, little doubt that the densities of the vapours of the alcohols and of most of the compound ethers correspond with theory at all temperatures, but the singular anomalies presented by the acetic, formic, and sulphuric acids, and by the perchloride of phosphorus and some essential oils, show with what circumspection we must adopt the theoretical number as truly representing the density of any vapour near its point of condensation. Some of the irregularities in the results now given, may perhaps be traced to this cause.

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Dec. 20, 1847.

Thomas Graham, Esq., Vice-President, in the chair.

Professor Dana presented a copy of his memoir "On certain laws of cohesive attraction," to the Library. Messrs. Charles W. Swaisland, J. C. Stevenson, Henry Watts, B.A., Edward Frankland, William Payne, Robert Galloway, and W. E. Heathfield, were duly elected members of the Society.

The following communications were read :

*On the power of low pressure steam in charring animal and vegetable matter, and on the reducing power of charcoal at that temperature, by WILLIAM FERGUSON, Esq.*—An unsound steam-engine boiler having been covered with patent felt, to prevent radiation from its surface, the felt was observed, at the expiration of five or six months, to have become charred wherever the steam made its escape through the cracks of the boiler, whilst those parts of the felt which remained dry, although exposed to the same heat, were perfectly unaltered. The boiler was worked under a pressure of 6 lbs., which corresponds with a temperature of 232° F., but the temperature of the escaping steam and of those parts of the felt in contact with it, was 212° F. Another instance in which wood had been charred was observed in the float-gauge of a brewing-copper, which had been exposed during five years to the vapour and the saccharine solution, at a temperature not exceeding 215° or 216° F. The charcoal in this case was permeated by a soluble salt of copper, and the interstices were filled with octahedral and dodecahedral crystals of metallic copper. The author concludes, from the odour of pyroligneous acid which was perceptible, that acetic acid was formed by the decomposition of the wood, and that this united with the copper to form an acetate, which even at the temperature of 216° F., was partially reduced to the metallic state, whilst in intimate contact with the porous charcoal.

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V. *On the artificial formation of Crystalline Oxide of Zinc.* By  
MESSRS. WILLIAM and THORNTON J. HERAPATH.

It is to Mr. Cox, of the Patent Lime Works, Bristol, that we are indebted for the discovery of the remarkable and beautiful substance, which forms the subject of the present paper. Mr. Cox found it lining and partially filling up the anterior extremity of one of the earthenware retorts which had been used for the distillation of zinc at his manufactory.

It occurred as an aggregation of brilliant, prismatic, needle-shaped crystals, having a vitreous, semi-metallic lustre when viewed by reflected light, but transparent and colourless when examined by transmitted light. These crystals were so completely studded over with tubercles of various shapes and sizes, that it was only at the apices of a few of the larger ones that any traces of angles could be perceived, from which to judge of their original form. From these, however, it appeared that their form (as well as could be determined from such irregular crystals), was a four-sided, rectangular prism. Figs. 1 and 2 are illustrative of the appearance which they exhibited

FIG. 1.



FIG. 2.



under a magnifier of about 3 diameters. Occasionally a sword-shaped crystal was met with, having numerous smaller, irregular crystals proceeding from it at right angles to the edge, and plane with the surface of the crystal, Fig. 3.

The specific gravity of the larger and most perfect crystals was 5,5298.

FIG. 3.



They were exceedingly brittle, and the broken surfaces had a very perfect conchoidal fracture.

Their hardness was about 4·25.

They remained unaltered in appearance, even at a white heat, and did not lose in weight.

The crystals dissolved in nitric, hydrochloric, and dilute sulphuric acid, without effervescence, leaving a small quantity of a brilliant, crystalline residue, which when examined by a microscope of high power, was found to consist of transparent, colourless, crystalline fragments, possessing a very perfect conchoidal fracture, amongst which were scattered a few unbroken and very perfect rectangular prisms.

When analysed in the usual way, by solution in nitric acid, &c., the crystals yielded :

	I.	II.	III.	IV.
Protioxide of zinc . . .	88·45	89·40	91·84	92·05
Crystalline residue . . .	11·55	10·60	8·16	7·95
	100·00	100·00	100·00	100·00

These analyses show that they are not perfectly uniform in composition.

The crystalline residue being insoluble in all the mineral acids, and also in a boiling solution of caustic alkali, was analysed by the following process.

It was fused for about half an hour with an excess of caustic potash in a silver crucible, at a bright red heat. The fused mass was then extracted with boiling water, the solution treated with an excess of nitric acid, and the whole evaporated to dryness. Upon re-solution in dilute nitric acid, a quantity of peroxide of tin remained undissolved; this was collected on a filter, washed, ignited and weighed. The solution was then boiled with an excess of carbonate of potash, the precipitated carbonate of zinc collected on a filter, well washed with hot water, reduced to oxide by ignition in a platinum capsule, and weighed. Four analyses of this residue gave the following composition in 100 parts :

	Found by experiment.					Calculated.	
	I.	II.	III.	IV.	Mean.	Atoms.	
Stannic acid . .	63·592	65·634	66·002	66·265	65·373	1	64·912
Protoxide of zinc .	36·408	34·366	33·998	33·735	34·627	1	35·088
Stannate of zinc .	100·000	100·000	100·000	100·000	100·000	1	100·000

This substance may therefore be viewed as consisting of crystals of pure oxide of zinc, to which the smaller crystals of stannate of zinc acted as nuclei.

The crystals were probably produced by the slow percolation of atmospheric air, either through a small crack in the retort, or perhaps through the porous sides of the retort itself; the oxygen of the air gradually combining with the red hot vapour of the zinc formed a non-volatile oxide, which being very slowly deposited, assumed the crystalline form.

Jan. 17, 1848.

The President in the chair.

Messrs. Herapath presented specimens of the crystals of oxide of zinc, which had formed the subject of their paper, to the Society's Museum. Dr. Daubeny presented his work on Volcanoes to the Library. Messrs. William Odling, Robert Beavan, and Benjamin Cooper, were elected members of the Society.

The following papers were read :

*On the quantitative estimation of phosphoric acid, and on its presence in some of the marls of the upper green sand formation, by J. C. NESBIT, Esq., F.G.S.—*The methods proposed by Fresenius for estimating the quantity of phosphoric acid in a solution containing iron and alumina, have been tested by Mr. Nesbit, upon the occasion of the analysis of these marls. The ammonio-magnesian phosphate precipitated by a mixture of sulphate of magnesia, chloride of ammonium and caustic ammonia (phosphoric acid test), from the solution of the phosphates of iron and alumina in hydrochloric acid, ammonia, and tartaric acid, was frequently found contaminated with a variable quantity of alumina and oxide of iron, which appeared to depend upon the degree of concentration of the liquid, and upon the amount of tartaric acid which it contained. The author succeeded in avoiding this source of error by diluting the solution of the phosphates until it assumed a light straw colour, and by employing a large quantity of tartaric acid and a very considerable excess of ammonia. The appearance of the precipitate on the addition of the phosphoric acid test may also in some measure be

taken as a guide ; for, if the precipitate at the expiration of twenty-four hours, during which time it should always be allowed to stand, be either flocculent or gelatinous, instead of crystalline, the presence of iron or alumina may generally be predicated in it. When the foregoing precautions were observed, the results were found to be very nearly accurate, and iron could only be detected in the precipitate by sulphocyanide of potassium. In cases where doubt may arise as to the purity of the precipitate, it should be re-dissolved with the addition of a little tartaric acid, and again precipitated by ammonia.

The other plan for the estimation of phosphoric acid recommended by Fresenius, according to which the solution of the phosphates of iron and alumina in hydrochloric acid is mixed with ammonia until a precipitate begins to form, when the whole is boiled with acetic acid and acetate of soda in excess (or in cases where no iron is present in the solution, with the addition of perchloride of iron), is found by the author to be inapplicable when phosphate of alumina is contained in the solution. All the phosphoric acid contained in the solution is precipitated in combination with iron and alumina on boiling the above mixture, and by the addition of ammonia and hydrosulphuret of ammonium to the solution of the precipitate in hydrochloric acid, the iron and alumina are separated, leaving, according to Fresenius, the whole of the phosphoric acid in combination with ammonia in the filtrate. When alumina is present, Mr. Nesbit finds that phosphoric acid is kept back in the precipitate formed by ammonia and hydrosulphuret of ammonium, and cannot be obtained in the filtrate ; he, therefore, rejects the process as fallacious, except in those cases where alumina is absent.

The marl examined is remarkable for containing a large amount of phosphoric acid, the average quantity deduced from the experiments being 2·31 per cent.

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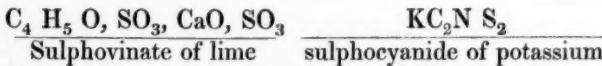
*VI. On Hyposulphathylic, Hyposulphamethylic, Bisulphithylic and Bisulphimethylic Acids, produced by the action of nitric acid upon the Sulphocyanides and Bisulphides of Ethyl and Methyl, &c. By SHERIDAN MUSPRATT, PH. D.*

The action of nitric acid upon mercaptan and the bisulphide of ethyl has been studied by Löwig, Weidmann, and Kopp, who found that the same acid was produced from the two substances. In the former, an atom of hydrogen was removed and four of oxygen entered into combination ; while with the latter the hydrogen remained intact, and four atoms of oxygen were assumed :

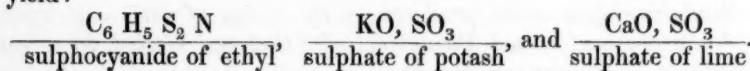
Mercaptan . . . . .	C <sub>4</sub> H <sub>6</sub> S <sub>2</sub>
Bisulphide of ethyl . . . . .	C <sub>4</sub> H <sub>5</sub> S <sub>2</sub> .
Bisulphithylic acid . . . . .	C <sub>4</sub> H <sub>5</sub> S <sub>2</sub> O <sub>4</sub>

Bisulphithylic acid gives crystallizable salts with all the bases which are described in the interesting memoirs\* of the above-cited chemists. The action of nitric acid upon the sulphocyanogen compounds of ethyl and methyl has been, up to the present time unknown, and it was possibly this circumstance that induced my much esteemed preceptor and friend, Baron Liebig, to suggest the investigation to me. A careful examination of the subject has led to the discovery of two new acids, which are formed in a very remarkable manner. When a new acid is obtained in the ethyl series, we may, with a degree of certainty, assume the existence of a corresponding one in the methyl class of bodies; and although the latter series is not as yet so extended as the former, still the analogues of all the sulphur and oxygen compounds of the ethyl combinations, will, I am convinced, before long be brought to light, and *vice versa*; and as soon as this is the case, more definite conclusions may be drawn by chemists with regard to the basyles and salt radicals, upon which the whole fabric of chemical theory is at present based.

*Preparation of sulphocyanide of ethyl.*—It is very difficult to obtain this body in large quantities. The best method of preparing it is by distilling in a retort equal measures of strong solutions of sulphovinate of lime and sulphocyanide of potassium. The capacity of the retort must be twelve times that of the space occupied by the mixture, so as to prevent any of the solution passing over into the receiver, which it is very apt to do, owing to a violent intumescence that occurs at intervals. The decomposition which takes place may be represented by the annexed equation :



yield :



Sulphocyanide of ethyl, discovered by Liebig and studied by Cahours,† is an oily and very dense liquid, possessing an odour of garlic. The latter chemist states in his Treatise, that "pretty-concentrated nitric acid dissolves it with the aid of heat; but that upon cooling, it separates again completely." I cannot imagine how so accurate an investigator as M. Cahours could have made this mistake. Rather strong nitric acid decomposes the sulphocyanides

\* Löwig's Organic Chemistry, vol. II. p. 427, and Poggendorff's Ann. der Phys. und Chem. Bd. XLVII. p. 153.

† Ann. der Pharm. 61-2, p. 99.

of ethyl and methyl with great rapidity, affording acids which will be subsequently described.

*Process for obtaining hyposulphathylic acid.*—About an ounce and a half of sulphocyanide of ethyl and the same quantity of tolerably concentrated nitric acid were introduced into a retort, connected with one of Liebig's condensers. A slight heat was applied to the retort during the whole process. At first the action was very brisk, and attended by the evolution of nitrous fumes, carbonic acid, and nitric oxide. Sulphuric acid was also formed during the operation; the quantity, however, depended upon the concentration of the acid employed. If weak nitric acid is used, traces only of sulphuric acid can be detected in the liquid. The distillate was repeatedly returned to the retort, so that very little loss of oil was sustained. The menstruum, after four or five distillations, was poured into a porcelain basin, and evaporated in a water-bath until the last trace of nitric acid was expelled. A fluid, like oil of vitriol, remained, possessing a slight alliaceous odour. This was diluted with water, in which it readily dissolved, saturated with carbonate of barytes, and filtered to remove the excess of carbonate and any sulphate of barytes. The filtrate, when evaporated very slowly, afforded large crystals of hyposulphathylate of barytes. These crystals were dissolved in water, precipitated by an excess of absolute alcohol, and re-crystallized. The acid may be obtained in a state of purity by precipitating the barytes with sulphuric acid from the aqueous solution of the salt, filtering, digesting the filtrate with carbonate of lead, re-filtering and decomposing the solution containing the lead salt by hydro-sulphuric acid. When the sulphide of lead is separated and the filtrate evaporated in a water-bath, the acid is left in a pure state.

*Properties of the acid.*—When the acid is fused with potash and the residue treated with sulphuric or muriatic acid, large quantities of sulphurous acid are evolved. It withstands a very high temperature before suffering decomposition; fumes of sulphuric acid first escape, and then sulphurous acid is eliminated. The taste of the acid is most disagreeable and acrid, and of this the salts, all of which are soluble, also partake. The acid is miscible with water and alcohol in all proportions, and is very persistent.

*Hyposulphathylate of barytes.*—This salt is so very soluble in water, that it can only be obtained in fine rhombohedral prisms by allowing a concentrated solution to evaporate slowly. It is also very soluble in spirits of wine and ether, but insoluble in alcohol, which throws it down in beautiful satiny crystals. It parts with its water at  $212^{\circ}$ . The dried crystals, when heated with soda-lime, gave no

indications of ammonia ; fused with potassium and tested with iron solutions, the absence of nitrogen was fully proved ; and this is the most remarkable feature with regard to the acid. In what form was the nitrogen of the sulphocyanide of ethyl eliminated ? Not as ammonia, for no trace of this alkali could be detected. It must have passed off in the form of nitric oxide or nitrous acid. No instance of similar decomposition has hitherto been observed, *i. e.* an acid containing *no nitrogen* has never yet been produced by the action of one nitrogenous body upon another.

- I. 0·4140 grms. of the salt dried at 212° and burned with chromate of lead afforded : 0·2090 grms. carbonic acid and 0·1200 grms. of water.  
 II. 0·4763 grms. of the salt gave : 0·2300 grms. carbonic acid, and 0·1310 grms. of water.  
 I. 0·2560 grms. of the salt gave : 0·1665 grms. sulphate of barytes = 0·1093 grms. barytes.  
 0·4190 grms. of the salt treated with potash and nitre gave : 0·5495 grms. sulphate of barytes = 0·0753 grms. sulphur.  
 II. 0·4160 grms. of the salt gave : 0·2750 sulphate of barytes = 0·1800 grms. barytes.  
 0·2340 grms. of the salt gave : 0·3000 grms. sulphate of barytes = 0·0411 grms. sulphur.

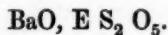
Centesimally represented :

	Theory.	Experiment.		Mean.
		I.	II.	
4 eq. Carbon . . .	24·00	13·52	13·76	13·46
5 „ Hydrogen . . .	5·00	2·81	3·21	3·13
2 „ Sulphur . . .	32·00	18·01	17·99	17·77
5 „ Oxygen . . .	40·00	22·54	22·35	22·66
1 „ Barytes . . .	76·60	43·13	42·69	42·98
	177·60	100·00	100·00	100·00

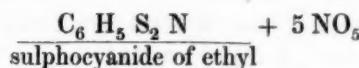
The following formulæ agree very well with the above results :



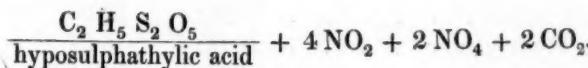
or,



The decomposition that takes place when nitric acid acts upon sulphocyanide of ethyl may therefore be represented by the annexed equation :



yield :



0·7270 grm. salt, dried at 212°, gave : 0·0365 grm. water, which is equivalent to :

	Theory.	Exp <sup>t</sup> .
1 eq. hyposulphathylate of barytes	177·60	95·16
1 „ water . . . . .	9·00	4·84
	<u>186·60</u>	<u>100·00</u>

Formula : BaO, C<sub>4</sub>H<sub>5</sub>S<sub>2</sub>O<sub>5</sub> + aq.

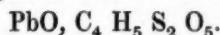
The barytes salt, when heated in a tube, blackens and gives off fumes possessing a most stifling smell.

*Hyposulphathylate of lead.*—This salt crystallizes from a hot, concentrated solution in beautiful colourless plates, which are extremely soluble in water, spirits, and alcohol. They intumesce when heated, and the residue contains sulphide of lead.

0·2790 grm. of dried salt gave : 0·0000 grm. sulphate of lead = 0·1472 grm. ox. lead, corresponding to :

	Theory.	Exp <sup>t</sup> .
1 eq. hyposulphathylic acid . . .	101·00	47·41
1 „ oxide of lead . . . . .	112·00	52·59
	<u>213·00</u>	<u>52·76</u>

The preceding results agree with the formula :



0·6110 grm. dried over sulphuric acid, and heated at 212°, gave : 0·0250 grm. water, corresponding to :

	Theory.	Exp <sup>t</sup> .
1 eq. hyposulphathylate of lead	213·00	95·98
1 „ water . . . . .	9·00	4·02
	<u>222·00</u>	<u>100·00</u>

Formula : PbO, C<sub>2</sub>H<sub>5</sub>S<sub>2</sub>O<sub>5</sub>, + aq.

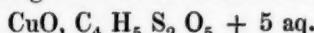
*Hyposulphathylate of copper.*—It is very difficult to obtain this salt in well-defined crystals, on account of its great solubility in water and spirits. When the crystals are heated in a tube, they intumesce, and as soon as they blacken, vapours are evolved, possessing a most disagreeable odour.

0·2020 grm. of this salt dried over sulphuric acid, yielded : 0·0970 grm. carbonic acid, and 0·0880 grm. water.

0·6170 grm. of the salt gave : 0·1338 grm. oxide of copper, which, centesimally represented, is equivalent to :

	Theory.	Exp <sup>t</sup> .
4 eq. Carbon . . . . .	24·00	12·90
10 „ Hydrogen . . . . .	10·00	5·37
2 „ Sulphur . . . . .	32·00	17·20
10 „ Oxygen . . . . .	80·00	43·03
1 „ Oxide of copper . . . . .	40·00	21·50
	<hr/> 186·00	<hr/> 100·00

The annexed formula agrees with the above numerical results :



I thought it would be very interesting, if by acting upon the sulphocyanide of ethyl with chlorate of potash, the same acid as the one just described could be produced. When sulphocyanide of ethyl is gradually added to a mixture of chlorate of potash and hydrochloric acid, a very violent action takes place, which is sometimes so brisk as to inflame the volatile products. As soon as the oil had entirely disappeared, the liquid was placed in a water-bath and evaporated to dryness, in order to get rid of the excess of hydrochloric acid. The residue was then treated with absolute alcohol, in which medium the chloride of potassium and any sulphate of potash are insoluble. When this solution was filtered and the filtrate evaporated on a water-bath, an oily acid was left, which was saturated with carbonate of barytes, and the whole again filtered. The solution that passed through, gave beautiful silky crystals, with absolute alcohol, possessing all the appearance of the hyposulphathylate of baryta. There was not enough of the salt for a combustion ; I consequently only made a determination of the barytes :

0·1060 grm. of salt, dried at 212°, gave : 0·0685 grm. of sulphate of barytes = ·0450 grm. barytes.

The above result affords 42·45 per cent of barytes, and the formula



requires 43·13 per cent. I have, therefore, no doubt, that the acid is the same as that produced by the action of nitric acid upon the sulphocyanide of ethyl. One equivalent of sulphocyanide of ethyl, three equivalents of chlorate of potash, and seven equivalents of hydrochloric acid, contain the elements of one equivalent of hyposulphathyllic acid, two equivalents of carbonic acid, one equivalent of nitric oxide, three equivalents of chloride of potassium, seven equivalents of water, and seven equivalents of free chlorine.

The sulphocyanide of ethyl is readily acted upon by chlorine gas.

When a stream of the gas is passed through it for some time, large quantities of chloride of cyanogen are formed, and there subsides a heavy yellow oil, which disappears when repeatedly washed. I have not further investigated this reaction. When a cold alcoholic solution of potash is mixed with sulphocyanide of ethyl, and the mixture is allowed to stand for some days in a corked vessel, decomposition takes place. The liquid becomes blood-red, and acquires a most singular odour; but there are no indications of the presence of ammonia. The results of the above decompositions will be embraced in a treatise on the action of chlorine, bromine, potash, &c., upon the sulphocyanides of ethyl and methyl.

Before commencing the corresponding reactions in the methyl series, I prepared Löwig's acid from the bisulphide of ethyl. The combustion of its copper salt dried at  $212^{\circ}$ , afforded me the following results :

0·3765 grm. salt, burned with chromate of lead, gave : 0·2000 grm. carbonic acid, and 0·1730 grm. water, numbers agreeing perfectly with Löwig's formula :

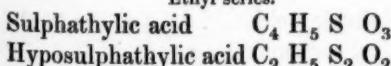


as may be seen from the annexed centesimal table :

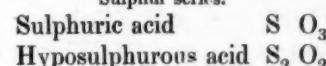
	Theory.	Löwig and Weidmann.	Muspratt.
4 eq. Carbon . . .	24·00	14·20	14·48
9 „ Hydrogen . . .	9·00	5·33	5·65
8 „ Oxygen . . .	64·00	37·94	36·47
2 „ Sulphur . . .	32·00	18·93	19·82
1 „ Oxide of copper .	40·00	23·60	23·28
	169·00	100·00	100·00

Thus we possess two more sulphur acids belonging to the ethyl series; the one, that of Löwig, obtained from the bisulphide of ethyl, and the other, by the action of nitric acid upon the sulphocyanide of ethyl. Is it not probable that the series may be still more extended, and that compounds may be produced, corresponding with the whole sulphur series of acids? *i. e.* by acting upon the higher sulphides of ethyl with oxidizing agents. In the following formulæ the known ethyl and sulphur acids are represented collaterally with those that are required to complete the series.

Ethyl series.



Sulphur series.



Ethyl series.		Sulphur series.	
Bisulphithylic acid	$C_4 H_5 S_2 O_2$	Bisulphurous acid	$S_2 O_4 ?$
Hyposulphathylic acid	$C_3 H_5 S_2 O_5$	Hyposulphuric acid	$S_2 O_5$
Tritrionathylic acid	$C_2 H_5 S_3 O_5 ?$	Tritrionic acid	$S_3 O_5$
Tetratrionathylic acid	$C_2 H_5 S_4 O_5 ?$	Tetratrionic acid	$S_4 O_5$
Pentatrionathylic acid	$C_2 H_5 S_5 O_5 ?$	Pentatrionic acid	$S_5 O_5$

*Preparation of sulphocyanide of methyl.*—This body is prepared in a similar manner to the ethyl compound. I distilled together equal quantities of strong solutions of sulphate of methyl and lime and sulphocyanide of potassium. The same precautions were observed as those described under sulphocyanide of ethyl. Sulphocyanide of methyl is a heavy oil, possessing a disagreeable alliaceous smell. It is very readily decomposed by strong nitric acid, yielding an analogous compound to the hyposulphathylic acid. The acid possesses no smell, and is not easily decomposed by heat.

*Hyposulphamethylate of baryta.*—The same course was followed for procuring this salt as with its analogue. It is very soluble in water, but is precipitated from that solvent in fine needles by spirits of wine and alcohol.

0·3640 grm. of the salt dried at 212°, and burned with chromate of lead, gave : 0·0965 grm. carbonic acid, and 0·0500 grm. water.

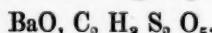
0·3385 grm. of the salt gave : 0·5200 grm. sulphate of barytes = 0·071 grm. sulphur.

0·2430 grm. of the salt gave : 0·0730 grm. sulphate of barytes = 0·1136 grm. barytes.

Centesimally represented :

	Theory.	Exp <sup>t</sup> .
2 eqs. Carbon . . . .	12·00	7·34
3 " Hydrogen . . . .	3·00	1·24
2 " Sulphur . . . .	32·00	19·56
5 " Oxygen . . . .	40·00	25·04
1 " Baryta . . . .	76·60	46·82
	163·60	100·00
		100·00

The preceding numerical results agree perfectly with the formula :



Hyposulphamethylate of barytes behaves like its analogue when heated in a test-tube ; water first passes off, and is followed by sulphuric and sulphurous acid fumes.

0·5325 grm. salt, dried over sulphuric acid and heated at 212° for two days, gave : 0·0278 grm water, corresponding to :

		Theory.	Exp <sup>t</sup> .
1 eq. Hyposulphamethylate of barytes	163·60	94·78	
1 „ Water . . . . .	9·00	5·22	5·25
	<u>172·60</u>	<u>100·00</u>	

Formula : BaO, C<sub>2</sub>H<sub>3</sub>S<sub>2</sub>O<sub>5</sub> + aq.

*Hyposulphamethylate of lead.*—This salt crystallizes in fine rhombic prisms from an aqueous solution. When heated, it gives off water with intumescence.

0·5745 grm. of the crystals gave : 0·0245 grm. water.

0·1755 grm. of the crystals gave : 0·1250 grm. sulphate of lead = 0·0921 grm. oxide of lead.

The composition in 100 parts is, therefore :

		Theory.	Exp <sup>t</sup> .
1 eq. Hyposulphamethylic acid	87·00	41·84	
1 „ Oxide of lead . . . . .	112·00	53·84	53·39
1 „ Water . . . . .	9·00	4·32	4·27
	<u>208·00</u>	<u>100·00</u>	

These numbers correspond with the formula :

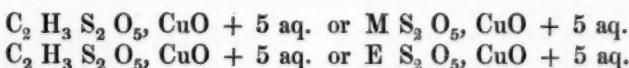
PbO, C<sub>2</sub>H<sub>3</sub>S<sub>2</sub>O<sub>5</sub> + aq.

*Hyposulphamethylate of copper.*—This salt is obtained in very fine crystals, by slowly evaporating the aqueous solution. It is remarkably soluble.

0·2514 grm. of the salt dried over sulphuric acid and burnt with chromate of lead gave : 0·0640 grm. carbonic acid, and 0·1130 grm. water, which numbers correspond with :

		Theory.	Exp <sup>t</sup> .
2 eq. Carbon . . . . .	12·00	6·98	6·94
8 „ Hydrogen . . . . .	8·00	4·65	4·99
2 „ Sulphur . . . . .	32·00	18·60	
10 „ Oxygen . . . . .	80·00	46·41	
1 „ Oxide of copper . . .	40·00	23·25	
	<u>172·00</u>	<u>100·00</u>	

This salt also agrees in composition with its analogue ; the two being represented by the annexed formulæ :



Previously to concluding my investigations on this subject, I wished to ascertain the composition of the acid resulting from the bisulphide of methyl, which has not hitherto been given. Cahours

states\* that tolerably concentrated nitric acid acts briskly upon the bisulphide of methyl, affording sulphuric acid collaterally with a peculiar acid, which yields crystals with potash, barytes, &c. In the preparation of the acid, I proceeded in the manner previously described. I remarked on evaporating the decomposed solution in the water-bath, that the fumes passing off were most stifling, and productive of lachrymation. The smell is similar to that of horse-radish, but much more disagreeable and pungent.

*Bisulphimethylate of lead.*—This salt crystallizes in fine rhombic prisms. When heated, penetrating vapours are expelled, accompanied by some water.

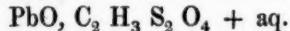
0·6960 grm. of the salt dried over sulphuric acid, gave : 0·1498 grm. carbonic acid, and 0·1265 water.

0·4040 grm. of the salt gave : 0·2980 grm. sulphate of lead = 0·2195 grm. oxide of lead.

Calculated per cent :

		Theory.	Exp <sup>t.</sup>
2 eq. Carbon . . . .	12·00	6·00	5·87
4 „ Hydrogen . . . .	4·00	2·00	2·01
2 „ Sulphur . . . .	32·00	16·00	
5 „ Oxygen . . . .	40·00	20·00	
1 „ Oxide of lead . .	112·00	56·00	54·33
	200·00	100·00	

The annexed formula may be deduced from the above :



Here then we possess another instance of the remarkable similarity which exists between the ethyl and methyl series of compounds ; for the above acid is the analogue of the bisulphithylic.

Before closing this memoir, I shall place some of the salts of the four acids in a tabular form, with the view of displaying the striking similarity existing between the two series :

Bisulphithylate of baryta	$\text{C}_4\text{H}_5\text{S}_2\text{O}_4$ , $\text{BaO} + \text{aq.}$
Bisulphithylate of lead	$\text{C}_4\text{H}_5\text{S}_2\text{O}_4$ , $\text{PbO} + \text{aq.}$
Bisulphithylate of copper	$\text{C}_4\text{H}_5\text{S}_2\text{O}_4$ , $\text{CuO} + 5 \text{ aq.}$
Hyposulphathylic of baryta	$\text{C}_4\text{H}_5\text{S}_2\text{O}_5$ , $\text{BaO} + \text{aq.}$
Hyposulphathylic of lead	$\text{C}_4\text{H}_5\text{S}_2\text{O}_5$ , $\text{PbO} + \text{aq.}$
Hyposulphathylic of copper	$\text{C}_4\text{H}_5\text{S}_2\text{O}_5$ , $\text{CuO} + 5 \text{ aq.}$
Bisulphimethylate of baryta	$\text{C}_2\text{H}_3\text{S}_2\text{O}_4$ , $\text{BaO} + \text{aq.?$
Bisulphimethylate of lead	$\text{C}_2\text{H}_3\text{S}_2\text{O}_4$ , $\text{PbO} + \text{aq.}$

\* Ann. de Pharm. 61-2, p. 93.

Bisulphimethylate of copper	$C_2 H_3 S_2 O_4$	CuO + aq. <sup>?</sup>
Hyposulphamethylate of baryta	$C_2 H_3 S_2 O_5$	BaO + aq.
Hyposulphamethylate of lead	$C_2 H_3 S_2 O_5$	PbO + aq.
Hyposulphamethylate of copper	$C_2 H_3 S_2 O_5$	CuO + 5 aq.

I hope that I shall soon be enabled to present this Society with another treatise upon these compounds.

VII. *Note on the constitution of the phosphates of the Organic Alkalies.* By THOMAS ANDERSON, M.D., *Lecturer on Chemistry, Edinburgh.*

The following observations were made a considerable time since, with the view of clearing up the apparent anomaly in the results obtained by Regnault\* in the analysis of the phosphate of strychnine, which he inferred to consist of single equivalents of phosphoric acid and strychnine, without any basic water, except the atom required by the organic base. As this result was entirely incompatible with the known constitution of the inorganic phosphates, it appeared to me desirable to ascertain its correctness; and it was my intention to have further extended the inquiry to the complete investigation of the phosphates of the organic alkaloids, but subjects of more interest having intervened, the analyses were laid aside until I should have leisure for extending and completing them, and they had almost escaped my memory, when my attention was recalled to them by the publication of a paper upon the constitution of the phosphates of aniline, by Mr. Nicholson.† At the conclusion of that paper, the author having stated his intention of further pursuing the subject, and investigating the phosphates of the other alkaloids, I again laid my analyses aside, in order that he might have the opportunity of completing what he had begun. As, however, more than a year and a half have now elapsed since Mr. Nicholson's paper was read to the Chemical Society, without the appearance of any further researches by that gentleman, I have resolved to publish my analyses, as a small addition to our knowledge of these salts.

*Phosphate of strychnine with one equivalent of strychnine.*—This salt is readily obtained by digesting a moderately dilute solution of tribasic phosphoric acid upon strychnine at a gentle heat, so long as it is freely dissolved. On allowing the solution to cool, the salt is leposited in groups of long radiated needles with truncated extre-

\* *Annales de Chimie et de Physique*, vol. 68, p. 150.

† *Memoirs of the Chemical Society of London*, Part 19, p. 227.

mities, which are easily obtained half an inch long, even from very small quantities of the solution. These crystals are acid to test-paper, and like all the salts of strychnine, excessively bitter to the taste. They dissolve in five or six times their weight of cold water, and in a much smaller quantity of hot. The analysis gave the following results.

I. 0·3228 grm. dried at 260° gave : 0·699 grm. carbonic acid, and 0·1735 grm. water.

II. 0·4535 grm. dried at 260° gave : 0·9765 grm. carbonic acid, and 0·2435 grm. water.

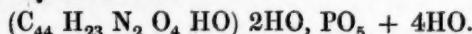
Which correspond with the following numbers per cent. :

	Experiment.		Calculation.		100.00	5567·3
	I.	II.	C <sub>44</sub>	H <sub>26</sub>		
Carbon . . . .	59·05	58·72	59·27	C <sub>44</sub>	3300·0	
Hydrogen . . . .	5·97	5·96	5·84	H <sub>26</sub>	325·0	
Nitrogen . . . .	"	"	6·28	N <sub>2</sub>	350·0	
Oxygen . . . .	"	"	12·58	O <sub>7</sub>	700·0	
Phosphoric acid . . . .	"	"	16·03	PO <sub>5</sub>	892·3	

The formula of the salt is therefore :



0·7516 grammes of crystallized phosphate of strychnine, heated to 260°, lost 0·0598 = 7·95 per cent, corresponding to 4 equivalents of water, the calculated result for which gives 7·42 per cent, and the formula of the crystallized salt is :

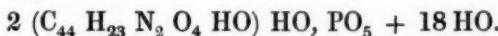


*Phosphate of strychnine with two equivalents of strychnine.*—If a solution of the salt just described be digested for a long time with an excess of strychnia in fine powder, an additional equivalent of the base is dissolved, and a new salt produced, which is deposited in crystals as the solution cools. In order to obtain it, however, very long continued digestion is necessary, and I have never succeeded in entirely converting the former salt into the latter, a considerable quantity of the acid salt always remaining in the solution. The separation of the two compounds is readily effected by two or three crystallizations, the acid salt being more soluble than that containing two equivalents of base. The latter is deposited from its solutions in the form of rectangular tables, often of considerable size, and sometimes so thin as to be beautifully iridescent. It is not acid to test-paper. The following are the results of the analysis :

0·2798 grm. dried at 260° gave: 0·6805 grm. carbonic acid, and 0·1649 grm. water.

	Experiment.		Calculation.	
Carbon . . . . .	66·31	66·64	C <sub>88</sub>	6600·0
Hydrogen . . . . .	6·54	6·18	H <sub>49</sub>	612·5
Nitrogen . . . . .	"	7·06	N <sub>4</sub>	700·0
Oxygen . . . . .	"	11·10	O <sub>11</sub>	1100·0
Phosphoric acid . . . . .	"	9·02	PO <sub>5</sub>	892·3
		100·00		9904·8

0·795 grammes, of the salt dried at 212°, at which temperature the whole of its water of crystallization is expelled, lost 0·143 = 17·6 per cent, corresponding exactly to 18 HO, the calculated result for which is likewise 17·6 per cent. These analyses give for the formula of the crystallized salt:



The foregoing analyses sufficiently prove that the phosphates of strychnine agree in constitution with the inorganic salts of the acid, and enable us to explain the source of error in Regnault's analysis. He obtained for his phosphate of strychnine :

Carbon . . . . .	59·85
Hydrogen . . . . .	5·85

in which result the excess of carbon is no doubt due to his having analysed the acid phosphate mixed with a small quantity of the last described salt, which owing to the long continued digestion necessary for its production in quantity, might easily escape detection unless actually sought for.

I endeavoured to prepare a double phosphate of strychnine and soda, by digesting strychnine in a solution of acid phosphate of soda; but did not succeed in obtaining it.

*Phosphate of brucine with two equivalents of brucine.*—When tri-basic phosphoric acid is digested upon brucine, rapid solution takes place; and on concentrating and cooling the solution, the salt in question is deposited, in short thick prisms, which have in general a somewhat yellowish colour. The salt is moderately soluble in cold water, and in all proportions in hot. It is neutral to test-paper. The crystals contain a large quantity of water of crystallization, which they lose by efflorescence in the air. When suddenly heated to 212°, they melt in their water, and then solidify into a resinous-looking mass, from which it is difficult to expel the remainder of the water.

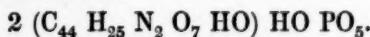
It is advisable, therefore, to remove the greater part of the water over sulphuric acid, and then to complete the drying at 212°.

The analysis gave the following results :

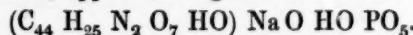
0·3545 grm. dried at 212° gave : 0·8065 grm. carbonic acid, and 0·208 grm. water.

	Experiment.	Calculation.	
Carbon . . . . .	62·05	62·53	C <sub>68</sub> 6600·0
Hydrogen . . . . .	6·51	6·27	H <sub>53</sub> 662·5
Nitrogen . . . . .	"	6·63	N <sub>4</sub> 700·0
Oxygen . . . . .	"	16·12	O <sub>17</sub> 1700·0
Phosphoric acid . . . . .	"	8·45	PO <sub>5</sub> 892·3
		100·00	10554·8

corresponding to the formula :



A double phosphate of brucine and soda is readily prepared by digesting brucine with acid phosphate of soda. It crystallizes in short opaque prisms. I was unable to obtain it perfectly pure, but the analysis gave results, approximating to the formula :

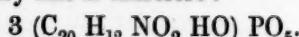


*Phosphate of quinine with three equivalents of quinine.*—Quinine dissolves with great rapidity in warm phosphoric acid, and on cooling, the fluid becomes a solid mass of minute needle-shaped crystals. If the solution be more dilute, it deposits the salt in the form of radiated tufts of silky needles, which are exceedingly thin and soft, and matt together into a mass as they become dry. The salt is perfectly neutral to test-paper. Analysis gave the following results :

0·334 grm. dried at 212° gave : 0·7575 grm. carbonic acid, and 0·205 grm. water.

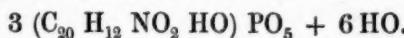
	Experiment.	Calculation.	
Carbon . . . . .	61·85	61·60	C <sub>60</sub> 4500·0
Hydrogen . . . . .	6·81	6·68	H <sub>39</sub> 487·5
Nitrogen . . . . .	"	7·18	N <sub>3</sub> 525·0
Oxygen . . . . .	"	12·32	O <sub>9</sub> 900·0
Phosphoric acid . . . . .	"	12·22	PO <sub>5</sub> 892·3
		100·00	7304·8

The formula of the dry salt is therefore :



0·548 grm. of the crystallized salt heated to 250°, lost 0·0415 = 7·57 per cent ; 0·4775 grm. heated to 250°, lost 0·0375 = 7·85 per

cent; six equivalents of water of crystallization correspond to .517 per cent, which gives for the crystallized salt the formula :



On another occasion I obtained a salt, the characters of which did not materially differ from those above described, but which lost by a heat of  $250^{\circ}$ , 15.3 per cent of water; this agrees with 12 equivalents of water, the calculation for which gives 15.6 per cent. It is probable, therefore, that two different hydrates of this salt exist.

The analyses of these salts are sufficient to establish in a satisfactory manner the general constitution of the phosphates of the organic alkalis, and to show that they agree with the inorganic salts of that acid as well as with the phosphates of aniline described by Nicholson. They contain, however, water of crystallization, which is absent in the phosphates of the latter base; and in this respect its salts correspond exactly with those of ammonia, while the phosphates of the fixed organic alkalis are more closely analogous to those of the inorganic bases. This peculiarity adds one to the numerous points of relationship subsisting among the volatile bases, and seems at the same time to point to some peculiarity of constitution distinguishing them from the non-volatile members of the class, which may perhaps be of more importance than it at first sight appears. It has always been considered that the organic bases formed an extremely well-marked natural family, agreeing perfectly in their functions and constitution; but this opinion has been arrived at principally from the observation of their general properties, and scarcely anything has been done in the way of minutely examining their compounds with the view of classifying them, or ascertaining the individual peculiarities of their constitution. The most minute attention has been paid to the examination of the salts of every new acid with the inorganic bases, and their constitution established with very great care, but the discoverer of a new organic base generally contents himself with the analysis of the platinum compound required to determine its atomic weight, and a few observations, sometimes very loose, on the characters of its other salts. It is true that the rarity of many of these substances and the difficulty and expense of obtaining them in sufficient quantity, almost preclude the possibility of a complete investigation; I apprehend, however, that if the same care which has been bestowed upon the salts with the view of characterizing their acid, were extended to them in relation to their basic constituent, it would afford an important means of classification, and even of indirectly determining the nature of their constitution.

The possibility of this is illustrated by the analyses detailed

above; for it so happens, that the bases whose salts I have examined, may be considered as representing three different classes, according to the number of equivalents of the alkaloid which unite with phosphoric acid to form what may be called its normal salt. Thus, if three portions of phosphoric acid be taken and digested under similar circumstances with quinine, brucine, and strychnine, three, two, and one equivalent of the respective bases will be dissolved. Quinine, therefore, which replaces at once three equivalents of basic water, may be compared to oxide of lead, or the oxides of the heavy metals generally. Brucine may represent the inorganic alkalis which replace two equivalents in their normal compound, while strychnine, which under ordinary circumstances replaces only a single equivalent of water, belongs to a class which has no analogue among the series of inorganic bases.

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Feb. 7, 1848.

The President in the chair.

Messrs. T. A. Malone, and J. B. Edwards, were duly elected members of the Society.

The following papers were read :

VIII. *On the products of the action of Potassium on Cyanide of Ethyl. By H. KOLBE, PH. D. and E. FRANKLAND, Esq.*

Professor Bunsen, in his investigation on the isolation of Cacodyl,\* points out two important conditions, which, in the separation, by means of metals, of the organic radicals from their liquid combinations, it is essentially necessary to observe. Firstly, the decomposition must be effected at a lower temperature than that at which the substance to be decomposed boils; and, secondly, the metallic compound produced must not be insoluble in the newly-formed radical.

These remarks induced us to make an experiment upon the separation of ethyl from its cyanide by means of potassium, as we conceived that this metal would exert its affinity for cyanogen at a temperature below the boiling point of that liquid.

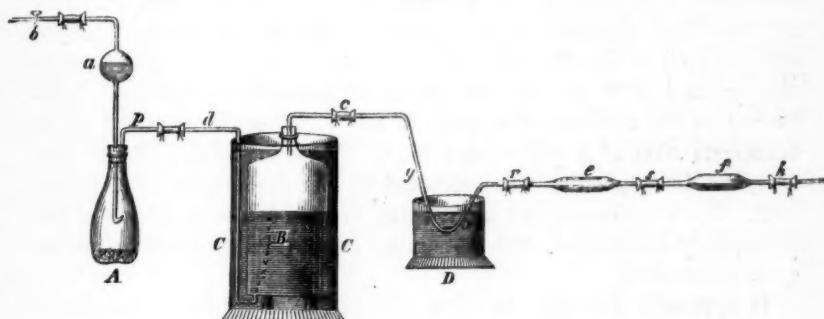
This expectation appeared to be fully realized. For, not only did the potassium act energetically upon the cyanogen compound, even at ordinary temperatures, but the cyanide of potassium which was formed in large quantity, was so completely dissolved in the sur-

\* *Annalen der Chemie*, Bd. 42, S. 45.

rounding liquid, that the metal retained a bright surface to the last. At the same time, an inflammable gas, insoluble in water, and possessing a faint ethereal odour, was evolved. We at first imagined this gas to be the radical sought, and we therefore resolved to follow out the investigation.

We employed the following apparatus, Fig 1, for the preparation of

FIG. 1.



the gas. In the flask *A*, which was capable of containing about 60 cubic centimetres, was placed a number of small pieces of potassium, previously freed from the adhering rock oil ; the neck was fitted with a cork, through which were inserted, on the one side, the gas-delivering tube *p*, and on the other, the tube *a* having a bulb blown upon it, the lower end being recurved and drawn out to a capillary orifice ; the upper extremity was connected by a caoutchouc joint with the stop-cock *b*. The bulb served to contain the cyanide of ethyl, which, by the cautious opening of the stop-cock *b*, could afterwards be allowed to fall in drops upon the potassium.

For the collection of the gas, the receiver *B*, inverted in the glass cylinder *C C*, was employed, its lower edge resting upon two strips of glass. The gas-delivering tube *g*, proceeding from the tubule of the bell-jar was slightly drawn out at *x*, and then connected by caoutchouc joints with the wider tubes *e f*, which served to contain the gas for eudiometric purposes. To the extremity of the last of these was attached a caoutchouc tube *h*, containing a piece of glass rod, by means of which the aperture could be perfectly closed.

Immediately before the experiment, and previous to the gas-delivering tube *d* being introduced under the bell-jar *B*, a quantity of boiled water, still warm, was poured into the outer cylinder *C C*, and suction being applied to the open extremity at *h*, the entire system of tubes from *B* to *h* was filled with it. The caoutchouc tube

surrounding the small piece of glass rod above mentioned, was then rendered perfectly air-tight by being tied with silk cord.

The first few drops of cyanide of ethyl, which, by the momentary opening of the stop-cock *b* were allowed to fall upon the potassium, exhibited generally a very violent action, which was not unfrequently attended by flashes of light, and accompanied, especially at the commencement, by a very rapid evolution of gas, which soon expelled all atmospheric air from the apparatus. As soon as the last traces of air had been displaced from the apparatus, the conducting tube *d* was inserted under the edge of the receiver *B*, which then became slowly filled with gas, as the pieces of potassium gradually disappeared on the addition of cyanide of ethyl and were converted into a tenaceous mass of a yellowish colour. Towards the end of the process, the decomposition was promoted by the application of a gentle heat. The experiment was interrupted as soon as the evolution of gas perceptibly diminished, the potassium being then, in most instances, quite consumed.

It appeared desirable to allow the gas collected in the bell-jar to stand over water for several hours, or even for a whole day, that the vapour of cyanide of ethyl, with which it was still contaminated, might be perfectly absorbed; we therefore took the precaution to cover the outer surface of the water with a layer of oil, in order to prevent the possibility of diffusion taking place between the enclosed gas and the atmosphere. The cylinder was afterwards quite filled with water, and the caoutchouc tube at *h* opened until all the water was expelled from the system of tubes, and its place was occupied by the gas acting under the pressure of the outer column of water.

The caoutchouc connectors *h*, *s*, and *r*, were then tied with silk cord, the two last doubly, and these being cut through between the ligatures, the tubes *e* and *f* were taken asunder. To make the four ends perfectly gas-tight, they were immersed in melted wax; by taking this precaution, gases may be preserved for a twelvemonth without any diffusion taking place; this method was preferred to fusing them before the blow-pipe, as it was to be feared that the heat necessary in the latter case might decompose the gas.

The rest of the gas was employed for the determination of its specific gravity, and for combustion with oxide of copper. For the first purpose we used a glass flask, containing about 200 cubic centimetres, the neck of which was contracted before the blow-pipe, until its diameter was reduced to that of a stout straw. This could be closed air-tight by means of a small ground-glass stopper.

In order to dry the gas, several pieces of fused potash were intro-

duced and fixed to the bottom of the flask by a gentle heat; it was then filled with mercury, inverted in the vessel *D* containing the same metal, and its open mouth held over the extremity of the gas-delivering tube, previously cut off at the point *x*. To overcome the pressure of the mercury, the gas in the receiver *B* was more strongly compressed by pouring a proportionate quantity of quicksilver into the outer cylinder. The gas was allowed to pour into the flask until the mercury in the neck stood only about 10<sup>mm</sup> above that in the vessel; the flask was then brought, with its mouth still immersed in the liquid metal, into a room of a constant temperature, where it was allowed to remain for upwards of an hour. Whilst the gas assumed the temperature of the surrounding air, which was ascertained by a delicate thermometer, it was at the same time perfectly dried by means of the pieces of fused potash. The height of the internal column of mercury was measured by a pair of compasses, and determined in millimeters. The flask was then carefully stopped under mercury and weighed, without bringing the hand in contact with it; it was afterwards filled with dry air, and lastly, with mercury, the weight being taken after each operation.

The following results were obtained:

Temperature of room . . . . .	19·7° C.
Height of barometer . . . . .	748·0 m. m.
Height of mercury in flask above that in outer vessel	17·2 m. m.
Weight of flask filled with gas . . . . .	53·591 grms.
Temperature in balance case . . . . .	20·3° C.
Weight of flask filled with dry air . . . . .	53·5775 grms.
Temperature of balance case . . . . .	20·9° C.
Capacity of flask . . . . .	210·2 c. c.

From which the specific gravity was calculated at 1·075.

For ascertaining the relative proportions of carbon and hydrogen, we allowed an indefinite volume of the gas to stream over ignited oxide of copper contained in a combustion tube, which was connected at one extremity with a chloride of calcium tube and potash apparatus, both previously weighed, and at the opposite end with another chloride of calcium tube connected with the gas apparatus *B* by the caoutchouc tube *c*. Thus the gas was freed from moisture before passing over the ignited oxide of copper. By carefully depressing the receiver *B*, a perfectly regular stream of gas was obtained, the velocity of which was indicated by the liquid in the potash apparatus.

When a sufficient quantity of water and carbonic acid had been formed, the caoutchouc tube *c* was divided, and the gases remaining in the combustion tube were drawn through the potash bulbs by

suction, in the usual manner. On re-weighing the chloride of calcium tube, it was found to have increased by 0·1794 grms.; the weight of the potash apparatus had increased 0·2915 grms. The gas consequently contained 0·0795 parts by weight of carbon to 0·0199 parts of hydrogen; numbers which closely correspond with the proportion C : H = 2 : 3.

The eudiometric analysis should confirm this result, and at the same time indicate the degree of condensation. For this purpose the gas contained in one of the tubes *e f* was employed, filled as before described, and transferred under mercury into the eudiometer and exploded with oxygen. For the details of the methods of observation in eudiometrical researches, and the precautions necessary to be used, we refer to the "Handwörterbuch der Chemie," article "Eudiometrie," vol. II. p. 1050.

## I.

	Observed vol.	Temp. C.	Height of mer- cury above that in trough.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Volume of gas used (moist) . . . .	117·2	15°·7	456·5 mm	743·9 mm 30·37
After admission of O (moist) . . . .	348·9	15°·7	216·3 , ,	743·5 , , 169·55
After combustion (moist) . . . .	224·5	16°·1	286·1 , ,	743·1 , , 94·00
After absorption of CO <sub>2</sub> (dry) . . . .	121·6	16°·2	451·5 , ,	744·4 , , 33·74
After admission of H (dry) . . . .	323·3	16°·3	241·4 , ,	744·0 , , 153·37
After combustion (dry)	167·4	16°·1	404·0 , ,	744·9 , , 53·90

## II.

Volume of gas used (moist) . . . .	68·7	15°·2	500·7 , ,	744·1 , , 15·00
After admission of O (moist) . . . .	331·9	15°·3	229·1 , ,	743·6 , , 157·65
After combustion (moist) . . . .	281·6	15°·3	280·9 , ,	744·1 , , 120·07
After absorption of CO <sub>2</sub> (dry) . . . .	231·6	15°·3	333·1 , ,	747·7 , , 90·92
After admission of H (dry) . . . .	539·0	15°·4	21·5 , ,	746·8 , , 370·05
After combustion (moist) . . . .	247·2	15°·4	316·7 , ,	745·5 , , 97·30

It appears from the above analyses that 1 volume of the gas requires  $3\frac{1}{2}$  volumes of oxygen for combustion, and generates 2 volumes of carbonic acid.

	Volume of gas used.	Oxygen consumed.	Carb. acid generated.
I.	30.37	106.02	60.26
	= 1 : 3.49 : 1.99		
II.	15.00	51.74	29.15
	= 1 : 3.45 : 1.94		

The above facts prove that the unknown gas has the composition and the state of condensation of the hitherto hypothetical radical methyl. The determination of its specific gravity, already detailed, gave the number 1.076, which agrees sufficiently near with the calculated specific gravity (1.037) when we consider that the gas, at the time the experiment was made, probably contained a little of the comparatively heavy cyanide of ethyl vapour.

$$\begin{array}{l} \text{1 vol. Carbon vapour} = 0.82922 \\ \text{3 vols. Hydrogen} = 0.20730 \\ \text{1 vol. Methyl gas} = \underline{1.03652} \\ \text{By experiment} \quad 1.076 \end{array}$$

Methyl is a colourless gas, not condensable at a temperature of  $18^{\circ}\text{C}$ . ( $65^{\circ}.5\text{ F.}$ ), insoluble in water, and possessing a slight ethereal odour. One volume of alcohol absorbs 1.13 volumes of this gas; agitated with an equal volume of previously boiled alcohol over mercury, it disappeared, with the exception of a small bubble, which did not amount to  $\frac{1}{2}$  per cent. Concentrated sulphuric acid had no action upon methyl, nor did it combine with sulphur or iodine when those elements were heated in the gas.

It appeared important to ascertain whether methyl, like hydrogen, would combine immediately with chlorine to form chloride of methyl. For this purpose we again filled some dried tubes, similar to those marked in the figure *e f*, and joined them with flexible connectors; to these a chloride of calcium tube was attached, connected with the caoutchouc tube *c*, which last was closed by a silken cord, while the receiver *B* was being filled with gas; the ligature was then loosed, and by pressing down the bell-jar, the gas was driven through the system of tubes. As the volume of gas in the receiver amounted to nearly twenty times the capacity of the tubes to be filled, we took for granted that all atmospheric air had been expelled from the apparatus. The tubes were then taken

asunder at the caoutchouc connections, in the manner before described.

Another tube, of the same dimensions as one of those above mentioned, was now filled with dry chlorine, and then connected as quickly as possible by a strong india-rubber joint, with a similar tube containing methyl, and the two gases were thus allowed to communicate with each other. After remaining for twenty-four hours, carefully preserved from the light, they perfectly intermingled, but were otherwise unchanged. On exposure to diffused daylight, the colour of the chlorine gradually disappeared, a proof that combination had taken place. After twenty-four hours more, the two tubes were hermetically sealed before the blow-pipe, and reserved for further experiments.

On breaking off the end of one of the tubes under mercury, it did not appear that any condensation had taken place, yet the new product could not be chloride of methyl, since a few bubbles of the gas which were allowed to escape contained a large quantity of hydrochloric acid.

To determine the quantity of hydrochloric acid present, we transferred the gas into a small eudiometer, and after carefully noting the volume, a ball of tribasic phosphate of soda was introduced, and afterwards one of caustic potash, which was allowed to remain until all traces of hydrochloric acid were absorbed; the volume was again read off, and the residual gas transferred to a large eudiometer, furnished in the usual manner with platinum wires, in which it was then exploded with oxygen, and yielded the following results.

#### ESTIMATION OF HYDROCHLORIC ACID.

	Observed volume.	Temp. C.	Height of mer- cury above C. that in trough.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Volume of gas used (dry) . . . .	103·6	18°·9	47·2 <sup>mm</sup>	752·5 <sup>mm</sup> 68·35
After absorption of H Cl (dry) . . .	55·1	18°·8	95·0,,	755·1,, 34·00

#### EXAMINATION OF THE GAS FREED FROM HYDROCHLORIC ACID.

Gas used (moist) . .	116·1	18°·8	439·2,,	755·0,,	32·50
After admission of O (moist) . . . .	362·5	19°·0	186·6,,	754·8,,	187·05

	Observed volume.	Temp. C.	Height of mer- cury above that in trough.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
After explosion* (moist)	281·5	19°·1	269·8 „ 753·7 „	123·00
After absorption of CO <sub>2</sub> (dry) . . .	186·1	19°·8	367·3 „ 753·2 „	66·95
After admission of H (dry) . . . .	462·3	20°·0	86·5 „ 752·4 „	286·90
After explosion (moist)	240·2	20°·0	311·6 „ 752·0 „	94·70

Owing to the great difficulty of obtaining the tubes for the methyl and chlorine of precisely the same size, and further, as in connecting them together it is impossible to prevent a small quantity of atmospheric air from being included, absolute correctness cannot be

\* The heat developed by the explosion was so great, that a portion of mercury was volatilized and the interior of the eudiometer was partially covered with a black film of the metal. At the same time a large quantity of free chlorine was evolved, which caused the residual gas to assume a deep yellow colour; it was, however, rapidly and perfectly absorbed by the mercury, converting the black film above mentioned into white bichloride of mercury.

According to Bunsen (*Annalen der Chemie*, Bd. 46, S. 33), the hydrogen of combustible gases containing chlorine should not be estimated by explosion with oxygen, since the hydrochloric acid evolved is partially decomposed with the separation of chlorine. If, as the results prove, a complete combustion has taken place in the above analysis, then the cause of this phenomenon unquestionably depends upon the high temperature accompanying the explosion of the gas. The following eudiometrical experiments show how very much the combustibility of hydrochloric acid is augmented by an increase of the heat developed during combustion; in these experiments hydrochloric acid was exploded with a mixture of oxygen and hydrogen, procured from the decomposition of water by voltaic agency, and free oxygen, in different proportions.

#### FIRST EXPERIMENT.

	Observed vol.	Temp. C.	Height of mer- cury above that in trough.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Oxygen gas (dry) . . .	172·3	21°·2	382·4 <sup>mm</sup> 748·9 <sup>mm</sup>	63·1
After admission of the gases composing water (dry) .	285·5	21°·2	265·9 „ 748·0 „	137·6
After admission of H Cl (dry)	362·2	21°·2	187·4 „ 746·9 „	202·7
After explosion (moist) .	237·7	21°·2	316·5 „ 746·9 „	102·3
After admission of water (moist) . . . .	170·0	21°·2	367·0 „ 746·9 „	61·2
			$\left( \begin{array}{l} + 1\cdot5^{\text{mm}} = \\ 21^{\text{mm}} \text{ pressure} \end{array} \right)$ of water.	

The explosion by means of the electric spark was in the above instance very slight, and the small quantity of chlorine separated could scarcely be distinguished by the colour it imparted to the gas. In the next experiment, where a smaller volume of

expected in the above analysis. The results, however, furnish data which enable us safely to fix the atomic constitution of the new chlorine compound.

It follows, then, that the mixture consisted of equal volumes of hydrochloric acid gas and of the other product. The explosion of the gas remaining after the absorption of carbonic acid with hydrogen, showed that it contained 2·8 vols. of nitrogen, the conversion of which into nitric acid during the explosion must have reduced the observed volume; the quantity of atmospheric air due to the above amount of nitrogen is 3·5 vols., which being deducted from 32·50, leaves 29·0 vols. of the true combustible gas; this, according to the analysis, consumed 90·5 vols. oxygen, forming with it 56·0 vols. carbonic acid.

Thus it has been shown, that 1 vol. of methyl gas with 1 vol. of chlorine is decomposed into 1 vol. of hydrochloric acid ( $= \frac{1}{2}$  vol. H +  $\frac{1}{2}$  vol. Cl) and into 1 vol. of another gas; the last must therefore evidently consist of  $\frac{1}{2}$  vol. chlorine and 1 vol. methyl, minus  $\frac{1}{2}$  vol. hydrogen, and its specific gravity must be 2·226.

hydrochloric acid gas was ignited with a much larger volume of the elements of water and less excess of oxygen than before, the explosion was attended with a much greater development of heat; there was at the same time a sublimation of the mercury and a copious separation of chlorine.

#### SECOND EXPERIMENT.

	Observed vol.	Temp. C.	Height of mer- cury above that in trough.	Barom.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
Constituents of water (dry).	305·4	21°·4	251·2 <sup>mm</sup>	746·8 <sup>mm</sup>	140·4
After admission of O (dry)	353·0	21°·5	199·8 „	746·2 „	178·8
After admission of H Cl (dry)	405·6	21°·4	146·1 „	745·8 „	225·6
After explosion (moist)	119·6	21°·5	435·2 „	742·9 „	32·0 <sup>f</sup>
After admission of water (moist) . . . . .	111·1	21°·5	419·8 „ $(+ 2^{\text{mm}} = 26^{\text{mm}})$ pressure of water	742·9 „	31·3

Although no absolutely exact results could be expected from these experiments, on account of the last reading being performed over water, yet they sufficiently demonstrate the point above alluded to.

By the first experiment, in which 65·1 vols. of hydrochloric acid were burnt with 74·5 vols. of the elements of water and 63·1 vols. of oxygen, only 1·9 vols. of this last disappeared. There were thus only 7·6 out of 65·1 vols. of hydrochloric acid decomposed. In the second experiment, 46·8 vols. of hydrochloric acid were mixed with 140·4 vols. of the constituents of water and 38·4 vols. of oxygen. On the explosion taking place, 7·1 vols. of oxygen disappeared. Out of 46·8 vols. of hydrochloric acid, only 18·4 vols. escaped decomposition. In the first instance, scarcely  $\frac{1}{3}$ ; in the second, above  $\frac{1}{3}$  of the volume of the acid gas was consumed.

1 vol. Carbon vapour . . . .	·82922
2½ vols. Hydrogen . . . .	·17270
½ vol. Chlorine . . . .	1·22445
Condensed to 1 vol. =	2·22637

This is the composition and state of condensation of chloride of ethyl, 1 vol. of which, according to calculation, requires 3·25 vols. of oxygen for complete combustion, and generates 2 vols. of carbonic acid; the above analysis sufficiently coincides with this calculation, 3·15 vols. of oxygen being consumed, and 1·93 vols. of carbonic acid generated by 1 vol. of the combustible gas.

Although this gas agrees closely with chloride of ethyl in its composition, in the state of condensation of its elements, and consequently in its specific gravity, yet it is not the same body, but a compound isomeric with it. For whilst chloride of ethyl becomes liquid at 12° C. and crystallizes at — 18° C., this gas, freed from hydrochloric acid by a ball of phosphate of soda, and from moisture by one of potash, retains its gaseous condition unchanged at the latter temperature. The two bodies also differ, though less decidedly in their relative solubility in water, which takes up an equal volume of chloride of ethyl, but absorbs at a temperature of 19° C. and a pressure of  $\frac{7}{8}$ m, nearly twice its volume of this gas.

It can scarcely be doubted, that this isomerism in a body having the rational composition of chloride of ethyl, is caused by the anomalous grouping of its atoms. It is possible that the new gaseous body is a conjugate compound of one atom of methyl with another atom of the same gas in which 1 eq. of hydrogen is replaced by chlorine  $C_2 H_3 + C_2 \left( \begin{smallmatrix} H_2 \\ Cl \end{smallmatrix} \right)$ . But how far this hypothesis is correct, further investigations must determine.

On the other hand, this gas exhibits several points of agreement with chloride of ethyl; it possesses a similar odour, burns with a green flame, generating hydrochloric acid vapour, and by exposure to sunlight with excess of chlorine, it is transformed like that compound into a substance resembling camphor, which is, without doubt sesquichloride of carbon  $C_2 Cl_3$ . Owing to the want of material, we have not further studied its properties.

#### KYANETHINE.

When 1 atom of methyl is obtained from 1 atom of cyanide of ethyl, the elements  $C_2 H_2 Cy$  remain, and must evidently be contained

in the tenaceous yellow mass, which in the preparation of methyl is left in the place of the potassium.

We have not, however, yet succeeded in ascertaining the combination into which this body, or at least the group  $C_2 H_2$  enters. When the residue is treated with water, a large quantity of cyanide of potassium is dissolved, and a white insoluble substance remains, which, as the following observations show, has no connection with the compound sought for.

This insoluble substance, which on account of its remarkable relations to cyanide of ethyl, had the first claim upon our attention, was freed from cyanide of potassium and cyanide of ethyl by washing with cold water, and then dissolved in boiling water. On cooling, small crystalline scales, of a pearl-like lustre were deposited; these dried at  $100^{\circ} C.$  exhibited the following composition.

I. ·3557 grms. burnt with oxide of copper\* gave ·856 grms. carbonic acid, and ·300 grms. water.

II. ·2055 grms. gave ·495 grms. carbonic acid, and ·171 grms. water.

The determination of the nitrogen was effected, according to Bunsen's method, by igniting an indefinite quantity of the substance with oxide of copper and metallic copper in a hermetically sealed glass tube, previously freed from nitrogen and exhausted.

By this process the following data were obtained :

	Observed vol.	Temp. C.	Height of mer- cury above that in trough.	Corrected vol. at $0^{\circ} C.$ and Barom. 1 <sup>m</sup> pressure.
Volume of mixed gases				
$CO_2 + N$ (moist) .	185·1	20°·9	370·4 mm	753·9 mm 62·81
After absorption of				
$CO_2$ (dry) . . .	40·8	20°·8	517·4 ,	755·8 , 9·04

Hence it follows, that the proportion of carbonic acid to nitrogen = 6 : 1·009.

Per centage composition : (C = 75 ; H = 12·5).

\* In this and the following analysis, after the termination of the combustion, a stream of oxygen was led over the reduced copper; this gas was furnished by heating a small quantity of fused perchlorate of potash placed at the posterior end of the combustion tube and separated from the oxide of copper by about  $\frac{1}{4}$  of an inch of recently ignited asbestos. Perchlorate of potash answers the purpose better than the chlorate, since the evolution of gas from the former is more regular, and less rapid, on the first application of heat. The potash apparatus was also furnished with a small tube containing a stick of fused potash, to absorb the aqueous vapour imbibed by the bubbles of gas in their passage through the potash ley; both were weighed together. Lastly, the

	Calculated.	Experiment.	
C <sub>6</sub>	65·5	65·6	65·6
H <sub>5</sub>	9·1	9·3	9·2
N	25·4	25·5	25·5
	100·0	100·4	100·3

The compound analyzed has, therefore, the composition of cyanide of ethyl ; it is, however, far from participating in any of its qualities. It dissolves in all acids with ease, forming with them in some cases beautiful crystallizable salts, which are soluble in water and alcohol ; from these it is precipitated unchanged by potash, ammonia, and the alkaline carbonates ; in short, it is an organic base. We propose to call it kyanethine, on account of its derivation from cyanide of ethyl. The formula of cyanide of ethyl does not, however, express the atomic constitution of kyanethine, but must be trebled in order to do so, as is proved by the analyses of its salts. One atom of the base, therefore, consists of C<sub>18</sub> H<sub>15</sub> N<sub>3</sub>.

Kyanethine is, when pure, a white volatile substance, inodorous, and almost tasteless ; it melts at about 190° C. (376° F.), and begins to boil at about 280° C. (536° F.), undergoing at the same time partial decomposition.

It is soluble in alcohol in almost all proportions ; it is very slightly soluble in cold, but tolerably so in hot water ; from the latter it separates, as was stated, by slow cooling in small, shining, crystalline scales. The solution in warm water shows a slight but distinct alkaline reaction. This base can be boiled with potash ley, without suffering the decomposition of cyanide of ethyl or undergoing any other change. When the ley containing it is evaporated to dryness, and the mass fused in a silver crucible, the greater part of the base sublimes without the separation of carbon.

Most of the salts of kyanethine have a bitter astringent taste, and are all soluble in alcohol and water.

Nitrate of kyanethine, C<sub>18</sub> H<sub>15</sub> N<sub>3</sub> + HO NO<sub>5</sub>, prepared by digest-

potash apparatus was detached from the chloride of calcium tube, and the oxygen which might possibly be still retained in the former, was displaced by atmospheric air.

Many compounds, rich in carbon, are not perfectly burnt by oxide of copper without the assistance of oxygen. Benzole, naphthaline, and similar volatile bodies give on an average  $\frac{1}{2}$  per cent. carbon too little ; but by the simultaneous use of oxygen, an extreme degree of accuracy is attained. The loss appears to be occasioned by the formation of a carburet of copper.

ing the base in dilute nitric acid, crystallizes by spontaneous evaporation in large colourless prisms; after re-crystallization it exhibits a perfectly neutral reaction. The analysis of this salt dried at 100° C. gave the following numbers :

·401 grms. gave ·699 grms. carbonic acid and ·256 grms. water.

Two determinations of nitrogen, according to Bunsen's method, yielded the following results :

### I.

	Observed vol.	Temp. C.	Height of mer- cury above C. that in trough.	Corrected vol. at 0° C. and 1 <sup>m</sup> pressure.
<b>Volume of mixed gases</b>				
CO <sub>2</sub> + N (moist) . . .	132·0	21°·2	134·6 mm	746·9 mm 72·74
After absorption of				
CO <sub>2</sub> (dry) . . .	28·2	21°·2	236·8 ,,	746·9 , 13·30

### II.

<b>Volume of mixed gases</b>				
(moist) . . . .	134·7	18°·4	130·0 ,,	745·3 , 75·76
After absorption of				
CO <sub>2</sub> (dry) . . . .	28·5	17°·9	235·0 ,,	750·9 , 13·80

Hence the proportion of carbonic acid to nitrogen :

I. 4·5 : 1·007

II. 4·5 : 1·002

Composition in 100 parts :

	Calculated.	Experiment.
C <sub>18</sub> . . .	47·4	47·5
H <sub>16</sub> . . .	7·0	7·0
N <sub>4</sub> . . .	24·5	24·6
O <sub>6</sub> . . .	21·1	
	100·0	

Sulphate and chloride of kyanethine are very soluble in water, and uncrystallizable. The acetate loses acetic acid by evaporation even in vacuo, and is changed into an insoluble basic compound. The oxalate, obtained by neutralizing oxalic acid with an excess of the base, gives large well-formed prismatic crystals, by spontaneous evaporation of the filtered liquor. The chlorocarbohyposulphate of kyanethine also shows a strong disposition to crystallize.

Like ammonia and the organic bases, chloride of kyanethine forms with chloride of platinum a double salt, of remarkable beauty, which separates in the form of a yellowish red crystalline precipitate when concentrated solutions of both salts are mixed. It is soluble in alcohol as well as in a mixture of alcohol and ether; in water it is difficultly soluble, and crystallizes by the slow evaporation of its watery solution in large ruby-red octohedrons. The alcoholic solution undergoes decomposition by boiling, and ammonio-chloride of platinum is subsequently formed.

The above precipitate, washed several times with water, pressed between blotting-paper, and dried at 100° C., gave on analysis the following numbers :

0·797 grm. moistened with alcohol, inflamed and afterwards strongly ignited, left 0·209 grm. platinum.

0·427 grm. gave 0·456 grm. carbonic acid and 0·169 grm. water.

Composition : Pt Cl<sub>2</sub> + C<sub>18</sub> H<sub>15</sub> N<sub>3</sub>, H Cl.

	Calculated.	Found.
C <sub>18</sub>	29·1	29·1
H <sub>16</sub>	4·3	4·4
N <sub>3</sub>	11·4	
Cl <sub>3</sub>	28·7	
Pt	26·5	26·2
		100·0

We have in vain endeavoured to discover the conditions which determine this remarkable transformation of the elements of cyanide of ethyl into kyanethine. All attempts to form this substance by other methods than the one already mentioned, have proved fruitless. Even when we altered the process only so far that, instead of allowing the cyanide of ethyl to fall in drops upon the potassium, the latter was thrown into that liquid, methyl gas was, it is true, formed, but scarcely a particle of this base. Cyanide of ethyl underwent just as little change when it was heated to 240° C. (464° F.) in a hermetically sealed glass tube, either alone or in conjunction with anhydrous cyanide of potassium. Lastly, the quantity of the base obtained by the above method was very small ; it amounted to only a trifling per centage of the cyanide of ethyl used.

It is difficult to form an opinion regarding the rational composition of kyanethine. But we may assume the hypothesis which has already been applied to aniline, and to which we have nothing to add,

viz., that it is like this substance, a conjugate amide, in which 2 eqs. of hydrogen are replaced by 2 eqs. of cyanogen  $C_{14} \left( \frac{H_{13}}{Cy_2} \right) + NH_2$ . The truth or fallacy of this view must be decided by further researches.

The above investigation was conducted in the laboratory of Prof. Bunsen, the use of which he, in the most friendly manner placed at our disposal during our stay in Marburg. We gladly avail ourselves of the present opportunity of expressing our warmest thanks for his uniform kindness towards us.

## NOTICES

OF

### PAPERS CONTAINED IN THE FOREIGN JOURNALS.

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*On the Acids of Sulphur.*\*—By acting upon the perchloride of sulphur with an aqueous solution of sulphurous acid, Messrs. Fordos and Gélis have succeeded in forming an acid of sulphur represented by the formula  $S_5O_8$ . This acid, which is isomeric with hyposulphurous acid, is obtained in combination with barytes, when the product afforded by the mutual action of the substances named above is freed from sulphuric and hydrochloric acids by carbonate of lead, and the filtrate, after the decomposition of the soluble lead-compound by sulphuric acid, is treated with carbonate of barytes, and precipitated by alcohol. The barytes salt, which crystallizes in needles, is decomposed by sulphuric acid, and the new acid, called by the authors pentathionic acid, is separated, and bears in its aqueous solution a great resemblance to the tetrathionic acid of the same chemists. The taste of the acid is slightly bitter, it reddens litmus paper, and undergoes the same decomposition as the barytes salt, which formed the principle subject of the present investigation. The barytes salt of this acid is completely converted into sulphate of barytes by chlorine, and the hypochlorites. It does not absorb iodine, and is thus distinguished from hyposulphurous acid, which is converted by that element into tetrathionic acid. Heated in a tube it yields sulphur, sulphurous acid, and sulphate of barytes, and in the hydrated condition, sulphuretted hydrogen gas. The solution of the salt in water is very instable, but acquires stability by the presence of alcohol, the last portions of which are difficultly separated from the salt, when it has been used for precipitating it from an aqueous solution. The formula for the salt is  $BaO, S_5O_8 + 2 HO$ .

The authors obtained the same acid by the action of sulphurous acid upon protochloride of sulphur; but are disposed to think that the sulphurous acid plays no active part in this decomposition, which is solely referable to the action of water upon the chlorides of sulphur, a more detailed investigation of which they are about to publish.

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*On the Analysis of the Oxygen Compounds of Sulphur.*†—As a means of estimating the amount of oxygen in the lower oxides of sulphur (phosphorus, arsenic, and antimony), and also the total amount of sulphur in

\* Ann. de Chim. et de Phy., xxii, 66.

† Ibid, xii, p. 60.

mixtures of the sulphur acids, Messrs. Fordos and Gélis recommend the use of a solution of an alkaline hypochlorite of known strength. The amount of liquid used, or the amount of chlorine absorbed, being equivalent to the quantity of oxygen required to raise the inferior oxide to the highest state of oxidation. Having found by experiment that all the lower oxides of sulphur, with the exception of hyposulphuric acid, are instantaneously decomposed in the cold by the hypochlorites, and that it is unnecessary to use an excess of the re-agent to ensure complete oxidation, the analysis is performed in the manner of a chlorometric assay.

The solution of the hypochlorite is prepared by passing chlorine to saturation through a weak solution of potash or soda, and diluting the product, until 1 decigramme of hyposulphite of soda requires exactly 25 cub. centimeters, or 50 measures of the liquid in the burette to convert it into sulphate: this quantity corresponding with 0.114 grm. of chlorine. The authors prefer acting upon a solution of 0.1 grm. of the substance to be analysed, in 100 grms. of water, the solution is slightly acidulated previous to the addition of the hypochlorite, and the least excess of the re-agent is then recognised by the odour of chlorine which is evolved when it ceases to be absorbed, or by a solution of indigo, as in the chlorometric process. The quantity of sulphur in a mixture of sulphur acids, is calculated from the amount of sulphuric acid produced by the action of the hypochlorite.

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*Analysis of the supposed double salt of Oxalate of Bismuth and Potash.\*—* The product obtained by boiling oxide of bismuth with binoxalate of potash, has been found by Dr. Schwartzenberg to contain a mere trace of potash, and to consist of oxalate of bismuth with water of crystallization. The salt was analysed by combustion with chromate of lead, and afforded :

	I.	II.	Atoms.	Calculated.
Carbon . . . . .	8·93	9·31	6	9·45
Hydrogen . . . . .	1·01	1·01	4	1·05
Oxygen . . . . .	28·03	27·65	13	27·31
Oxide of bismuth $\text{BiO}_3$	62·03	62·03	1	62·19
	100·00	100·00		100

agreeing with the formula :



*On Auriferous Glass.*—The interesting observations of Splittergerber upon white glass containing gold,† have been verified by Henry Rose;‡ but the remarkable changes which are produced in this glass by heat are attributed by the celebrated German chemist to other causes than those

\* Ann. der Chem. und Pharm., LXIV, p. 126.

† Pog. Ann. vol. 61, p. 144.

‡ Ibid. vol. 72, p. 556.

assigned them by the original observer. The glass upon which the experiments of Rose were performed, was prepared from a mixture of:

46 lbs. of quartz
12     "   borax
12     "   saltpetre
1     "   minium
1     "   white arsenic

which was moistened with the solution of 8 ducats in aqua regia, and then melted. The composition of glass from this mixture only differed from that used by Splittgerber, in containing no oxide of tin.

The glass acquired a ruby-red colour when heated in the air, or in an atmosphere of oxygen, carbonic acid, or even of hydrogen gas, in which latter case the red tint was not so intense, and the glass assumed a greyish hue, evidently from the reduction of the oxide of lead.

When exposed to a somewhat higher temperature, produced by transmitting a current of oxygen gas through a spirit-lamp, the glass became soft, and acquired a liver colour. The flame of the oxy-hydrogen blow-pipe fused the red glass into colourless beads, which could not, however, be re-converted into ruby glass by heat, as was the case in Splittgerber's experiments.

Splittgerber expressed as his opinion, with reference to the cause of these changes of colour, without attaching much importance to it, that the gold was contained in the colourless glass, in the state of a silicate of the peroxide, that the peroxide was reduced by the gentle heat to the state of oxide, and this it was that exerted the powerful colouring action, even when present in very minute quantity. Rose contends, that although the compounds of the oxide of gold are of a more stable character than those of the peroxide, yet it is highly improbable that a silicate of the peroxide should be reduced to the state of oxide by a lower degree of temperature than that at which it was formed, and more particularly as this is found to occur in an atmosphere of oxygen gas. He is, therefore, led to infer, that the colour is produced in the previously colourless glass, by the separation at a low temperature of a portion of the oxide of gold which had been combined at the higher temperature in the form of a neutral or acid silicate.

This opinion is borne out by the analogy presented by the oxides of copper. The ruby glass produced by means of the suboxide of copper, is also colourless when first prepared, and the colour is brought out by re-heating at a temperature below the softening point. That the glass does not become opaque by the separation of the oxide of gold, is explained by the minute quantity of the colouring oxide, just as very small quantities of suspended sulphuret of iron or sulphuret of lead will colour a liquid green or brown respectively, without impairing its transparency.

The resolution of the red into a liver-coloured glass at a higher tempera-

ture, which however is not sufficiently high to fuse the glass, is obviously the result of reduction, and this could not be effected, even at the heat of fusion, so long as the oxide of gold was in combination with silicic acid.

*Chemical examination of some specimens of Wine from the Rhingau.\*—*  
Dr. Fresenius has examined four of the most highly prized varieties of wine from the Rhingau, namely, 1. Hattenheimer, 2. Markobrunner, 3. Steinberger, and 4. Steinberger Auslese, all of the vintage of 1846.

The specimens of wine were prepared with the greatest care upon the plan of close fermentation. The examination commenced when they were four months old; the three former were perfectly clear; in the last, fermentation had not entirely ceased.

The investigation was undertaken for the purpose of determining the respective amounts of alcohol, sugar, free acid, and water, which they contained, and the total quantity of extractive matters.

1. The alcohol was separated from the wine by distillation, rectified over lime, and its quantity determined by the sp. gr. of the distillate.

2. The sugar remaining in the residue from distillation was determined, after careful evaporation, by the amount of carbonic acid which it evolved when mixed with a given quantity of yeast, at a temperature between 20° and 25° C. (68° to 77° F.), in the apparatus of Will and Fresenius.

3. The total amount of free acid (tartaric, malic, &c.) was estimated by the quantity of bicarbonate of soda, decomposed by a weighed quantity of the evaporated wine in the same apparatus.

4. Careful evaporation of weighed quantities of wine, and complete dessication of the residue at 100° C. (212° F.), gave the total amount of extractive matters.

The following were the quantities obtained from 100 parts:

	I.	II.	III.	IV.
Water . . . . .	85·079	83·681	84·384	78·275
Total extractive matter . . .	4·214	5·178	5·559	10·555
Anhydrous grape sugar . . .	3·580	4·521	4·491	8·628
Free acid expressed as free tartaric acid ( $\bar{T}$ , HO) . . .	0·556	0·533	0·497	0·424
Alcohol . . . . .	10·707	11·141	10·067	10·170

It may be deduced from these numbers that the juice of the grape, previous to fermentation, contained the following quantities of sugar in 100 parts:

	I.	II.	III.	IV.
Sugar, anhydrous $C_{12}H_{12}O_{12}$ .	24.52	26.25	24.12	28.46
Sugar, crystallized calculated $(C_{12}H_{12}O_{12} + 2 Aq.)$ . . . .	26.97	28.87	26.53	31.31

\* *Ann. der Chem. und Pharm.*, lxxiii, p. 384.

The value set upon these wines by judges, increases with the order of the specimens from I. to IV., and the following conclusions may consequently be drawn from the results :

1. The good quality of wine is in proportion :
  - a) to the small amount of free acid ;
  - b) to the actual quantity of sugar ;
  - c) to the amount of extractive matter which it contains.
2. The absolute amount of alcohol in wines of similar character is not of the first moment with reference to their respective qualities.
3. The specific gravity of wine is no criterion by which to estimate its quality.

It appears also from the foregoing examples, in which the amount of sugar varied considerably in the juice, whilst the alcohol was nearly the same in all the wines, that the temperature at which the fermentation is carried on exerts the greatest influence upon the amount of alcohol produced. When the largest quantity of alcohol has been produced from sugar corresponding with the temperature, all further action of the ferment upon the sugar is prevented by the presence of the alcohol. If the temperature is again raised, more alcohol is produced in proportion.

The after fermentation which frequently occurs in old wine is then accounted for by the author, upon the supposition, that the original amount of alcohol diminishes by keeping with the formation of different compounds of ethyl (tartaric and malic ether), and thus, so long as sugar and ferment exist in the wine, fermentation must proceed until the amount of alcohol sets a limit to its further production.

*On a new member of the series, resulting from the action of Chlorine upon Dutch liquid.\**—M. Isidore Pierre, by causing chlorine to act upon a considerable quantity of Dutch liquid, has succeeded in preparing the compound  $C_4 H Cl_5$  which was still wanting to complete the series resulting from the action of these bodies upon each other, in order to render it perfectly analogous to that obtained by Regnault from chloride of ethyl. This substance, which, to use the nomenclature of M. Regnault, may be called trichlorinated Dutch liquid, is obtained by a series of successive distillations of the product which passes over between the temperatures of  $145^{\circ}$  and  $160^{\circ}$  C. ( $293^{\circ}$ — $320^{\circ}$  F.), until the boiling point remains constant. The compound  $C_4 H Cl_5$  is liquid at a temperature of  $0^{\circ}$  ( $32^{\circ}$  F.); it boils at  $153^{\circ} 8$  C. ( $309^{\circ}$  F.) under a pressure of  $763^{mm} 35$ ,  $30 \cdot 05$  inches; its specific gravity at  $0^{\circ}$  C. ( $32^{\circ}$  F.) is  $1 \cdot 66267$ . It possesses an agreeable odour, and a sweet but hot taste, although in a less degree than Dutch liquid. The combining proportion of this compound, in the form of vapour, is 4 volumes, and the specific gravity of the vapour

\* *Annales de Chimie et de Physique*, xxii, 439.

is 7·101, by experiment it was found at 7·087. With a solution of potash in alcohol, it yields protochloride of carbon ( $C_4 Cl_4$ ) and chloride of potassium.

*On the Fatty Acids of Castor Oil.\**—Saalmüller has re-examined the fatty acids of castor oil, under the superintendence of Dr. Will, and is led to believe from his experiments, which however, are not perfectly conclusive, that the margaritic acid, discovered by Bussy and Lecanu in that oil, is probably stearic acid, and that the higher fusing point (130° C. 266° F.) and the difference of composition assigned it by the latter chemists, were probably occasioned by a portion of potash still remaining in combination with the specimens which they examined.

That portion of the fatty acids which, on the separation of the margaritic acid, remains fluid at ordinary temperatures, and was considered by Bussy and Lecanu as a mixture of ricinic with elaiodic acids, Saalmüller was unable to separate into two distinct acids, and he therefore considers it a simple acid, and has assigned it the name *ricinolic acid*, proposed in the first instance for elaiodic acid. This acid is prepared of constant composition from the residue, obtained by the process proposed by Gottlieb for the purification of oleic acid, after the separation of the margaritic acid. The fatty residue is saponified with an excess of ammonia, and the soap is decomposed with chloride of barium. The precipitated salt of barytes is washed with water, and dried at the temperature of the air upon a slab of gypsum; it is then redissolved in alcohol, from which it crystallizes on cooling, and is rendered perfectly pure by repeated recrystallization from the same solvent. The salt is decomposed by hydrochloric acid, and the acid is washed with water containing hydrochloric acid as long as any trace of baryta is taken up. The last portions of baryta are difficult of removal, and alcohol must not be applied during the decomposition, as it is subsequently nearly impossible to separate it completely from the acid.

The pure acid is of a light wine-yellow colour, and possesses, at ordinary temperatures, the consistence of syrup; it is colourless in thin layers, and has a powerfully acid taste, but no smell. Its specific gravity is 0·94 at 15° C. (59° F.), and it solidifies at a temperature of 60—10° C. (43°—50° F.), as a mass of rounded nodules. It is miscible in all proportions with alcohol and ether. The alcoholic solution has an acid re-action, and decomposes the carbonates of the alkalies with effervescence. The acid absorbs no oxygen from the atmosphere. It is decomposed when submitted to dry distillation, but, like the oil itself, affords no indications of the production of sebacic acid. The hydrated acid was analyzed by means of oxide of copper, and an excess of oxygen gas was necessary to effect complete combustion. The result was :

\* *Ann. der Chem. und Pharm.*, LXIV, 108.

	I.	II.	III.	Calculated.	Atoms.	
Carbon . .	73·06	73·16	73·45	73·08	38	228
Hydrogen . .	11·68	11·59	11·51	11·54	36	36
Oxygen . .	15·26	15·25	15·04	15·38	6	48
	100.00	100·00	100·00	100·00		312



The direct determination of the water in the hydrated acid yielded in two experiments 3·6 per cent. and 2·9 per cent., mean 3·25 water per cent. These results, in conjunction with the atomic weight deduced from the analysis of the barytic salt, leave no doubt concerning the composition of ricinolic acid, which is represented by the formula :  $C_{38}H_{55}O_5$ .

The salts of ricinolic acid, with the alkaline earths and the heavy metallic oxides, are nearly all crystallizable; they are all soluble in alcohol, and some are also soluble in ether. The salts do not alter by keeping; and like the acid, absorb no oxygen from the air. In addition to the salt of barytes, the salts formed with strontian, with lime, magnesia, oxide of zinc, oxide of lead, oxide of silver, and with oxide of ethyl, have been examined and described by the author.

The assertion of Boudet, that sulphurous acid is capable of converting the fatty oils, and amongst these castor oil, into solid bodies, in the same manner as is effected by nitrous acid, is not confirmed by the author, who was unable to produce any change in the nature or form of castor oil by the action of that gas. The gas was absorbed by the oil, but again completely removed by water.

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*On Carbothialdine.*\*—Messrs. Redtenbacher and Liebig have examined the action of sulphide of carbon upon ammonia-aldehyde. When pure ammonia-aldehyde is dissolved in alcohol, and sulphide of carbon is added to the liquid, the alkaline reaction of the latter is entirely destroyed, the mixture becomes warm and deposits in a few moments brilliant white crystals, which, when washed with alcohol, are pure carbothialdine.

This substance is insoluble in water and in cold ether, difficultly soluble in cold but readily soluble in boiling alcohol, from which it crystallizes unchanged; it is an organic base of the weakest kind, containing sulphur but no oxygen.

Carbothialdine forms a colourless solution with hydrochloric acid, from which ammonia and the fixed alkalies precipitate unaltered carbothialdine; but when this fluid is allowed to stand at rest for some time, it is converted into a yellowish-white gelatinous mass, and this is insoluble in water; boiled with an excess of hydrochloric acid, it is decomposed into sal ammoniac, sulphide of carbon and aldehyde.

When oxalic acid, and subsequently ether, are added to a hot solution

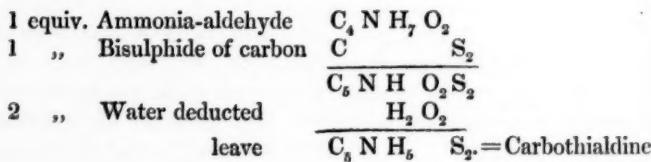
\* *Ann. der Chem. und Pharm.*, Lxv, p. 43.

of carbothialdine in alcohol, delicate, white, hair-like needles of oxalate of ammonia are immediately deposited.

A solution of silver produces a greenish-black precipitate in an alcoholic solution of carbothialdine, which becomes rapidly black and is converted into sulphuret of silver. Corrosive sublimate causes a thick curdy precipitate in the solution, of a yellowish-white colour, and copper salts afford a greenish precipitate. The analyses of this substance lead to the following composition :

		By experiment.
5 eq. Carbon . . .	30	37·04
1 " Nitrogen . . .	14	17·28
5 " Hydrogen . . .	5	6·17
2 " Sulphur . . .	32	39·51
	81	100·
		100·06

The formation of carbothialdine is therefore explained by the separation of 2 equivs. of water from the sum of the elements of ammonia-aldehyde and of sulphide of carbon :



*On some volatile products of the decomposition of albumen, fibrin, casein, and gelatine by means of peroxide of manganese or by chromic acid and sulphuric acid.\*—*An important investigation into the nature of the products of oxidation of casein, gelatine, and the constituents of the blood, fibrin and albumen, has been carried out by Guckelberger, with a view to throw some light on the so-called proteine compounds, the composition of which has given rise of late to so much discussion. It is now generally admitted, that albumen, fibrin, and casein, do not part with the whole of their sulphur when submitted to the action of potash; that, in fact, protein does not exist; and Guckelberger deduces from this fact, that the sulphur is contained in these bodies in two distinct forms of combination, the one of which is decomposed with the loss of its sulphur by potash, whilst the other is not; that the substances themselves are not simple compounds of a single group of atoms, or radical (protein) with sulphur, but are made up of several groups, which must be considered as proximate constituents of the compounds.

Elementary analysis is not calculated to throw light upon the constitution of such complex combinations as those here under consideration, and

\* *Ann. der Chem. und Pharm.*, LXIV. p. 39.

recourse must be had to the study of the products of their decomposition, a method which has been of such signal service in promoting our knowledge of other less complex substances, as may be instanced in the cases of amygdalin, salicin, &c.

*I. Oxidation of casein by peroxide of manganese and sulphuric acid.*—Purified casein was subjected to the action of peroxide of manganese and sulphuric acid, in a large glass retort; the proportions employed were;

1	part dried casein,
3	parts peroxide of manganese,
4½	„ oil of vitriol,
30	„ water,

The sulphuric acid was first diluted with twice its weight of water, and when the mixture had cooled down to a temperature between 40° and 50° C. (104°—122° F.), finely powdered casein was gradually added with constant agitation; it dissolved in the course of a few hours, and coloured the acid of a more or less intense brown or violet hue, according to the temperature. It was found advantageous to allow the mixture to stand until the following day, when it was diluted with the half of the requisite quantity of water and introduced into the distillatory vessel with the manganese. After complete mixture had been effected, the remainder of the water was added, and the distillation commenced. The retort must be large, as much froth is thrown up, and every possible means should be employed to secure perfect condensation, as even at a temperature of —15° (+5° F.) considerable loss is unavoidable.

The distillate possesses at first a peculiar and very acid smell, inciting cough and tears; when the half of the fluid has been distilled, this diminishes, and is at length replaced by an odour resembling that of oil of bitter almonds; a very small quantity of white flocculent matter is seen swimming in the nearly clear colourless fluid, which latter exhibits a powerfully acid reaction.

No trace of hydrocyanic acid could be detected in the distillate upon repeated trials.

To remove the acids, the liquid was shaken with chalk, and about the half of the liquid was distilled over. This product was perfectly neutral, but speedily became acid by exposure to the air. With ammonia and nitrate of silver, it exhibited the properties of aldehyde. Concentrated by repeated rectification, a milky liquid was at length obtained, upon which a layer of yellow oil floated, and this possessed the acrid smell mentioned above in the highest degree. The milky solution became clear after some time, and deposited in the cold a few drops of heavy oil, which was converted by exposure into a crystalline mass.

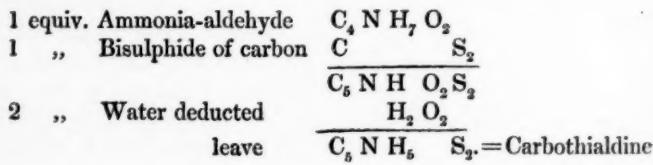
*a. Non-acid products.*—The yellow light oil was carefully distilled from a water-bath, and in order to separate the more volatile from the less volatile constituents, the flask containing it was connected with a long tube, bent at an angle of 120°. It began to boil at a temperature of

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40° C. (104° F.), and a perfectly colourless, very mobile liquid (i.) distilled over, miscible in all proportions with water, and possessing the entire choking properties of the oil. When the temperature of the water-bath had risen to 50° C. (122° F.), and the boiling had ceased, the receiver was changed; between 65° and 70° C. (149°—150° F.) ebullition began again, and the first portion which passed off, possessed the same choking smell as the former product; at a later period, however, an agreeable ethereal odour became perceptible, and the product was then collected in a separate vessel (ii.).

In the mean time the fluid in the flask had undergone an important change. The previously homogeneous liquid had separated into two, which were no longer miscible with each other; the one of these, comprising about 30 per cent. of the original quantity, was water, and upon this the other floated, in the form of a yellow oil. At the boiling temperature of water, a colourless oil passed over, which was very little soluble in water, floated on the surface, and smelt not unlike acetone (iii.).

When no further distillate was obtained at the temperature of the water-bath, the flask was exposed to an open fire, and the long bent tube exchanged for an ordinary short connecting tube. The product from this operation still swam at first upon the surface of the water, but a smell of bitter-almond oil became more and more perceptible, and the receivers were changed until the globules of oil which passed over subsided to the bottom of the accompanying water (iv.).

The product (i) of distillation, at a temperature between 40° or 50° C. (104°—122° F.), was found to be identical, both in composition and properties with aldehyde; its formula was therefore,  $C_4H_4O_2$ .

The second product (ii), which passed over at a temperature between 55° and 70° C. (131°—158° F.), was a colourless liquid with an agreeable ethereal smell, of 0·79 sp. gr. at + 15° C. (59° F.), miscible in all proportions with water, alcohol, and ether. It was perfectly neutral to test-paper, but became slowly acid when exposed to the air, and more quickly under the action of platinum-black; caustic potash produced no visible change in the liquid, and no metallic mirror could be obtained from it with nitrate of silver. This latter reaction proved the entire absence of the aldehyde of acetic acid. The composition of this body, deduced from experiment, is best represented by the formula  $C_3H_3O$ . It is therefore isomeric with acetone; but the author is disposed to consider it the aldehyde of metacetonic acid, or perhaps the hydrate of metacetone. If one equivalent of the substance is represented by 4 vol. of vapour, the weight of its vapour will be = 2·0105, and its formula,  $C_6H_6O_2$ .

6 vol Carbon . . .	4·9920
12 „ Hydrogen . . .	0·8316
2 „ Oxygen . . .	2·2186
	<hr/>
	8·3422
	4
	2·0105

The experimental result of the determination of the weight of the vapour gave the number 2·169.

The third product of distillation (III) is distinguished from the former two by its slight solubility in water; it boils between 68° and 73° C. (155°—163° F.). It is a clear liquid, with an ethereal but penetrating smell; its taste is burning and not unlike that of aldehyde. The specific gravity at + 15° C. (59° F.) was 0·8. It is soluble in all proportions in alcohol and ether, is neutral to test-paper, but becomes rapidly acid by exposure to the air. It exhibits the same reaction with alkalies and ammonia as aldehyde, and produces a brilliant coating of metallic silver with a silver solution. Sulphuric acid affords a deep blood-red colour with this substance, but no precipitation of carbon is apparent. The analyses with oxide of copper led to the formula,  $C_4H_4O$ , but the constitution of the compound which it forms with ammonia, as well as that of the acid into which it is resolved by oxidation, clearly prove that its equivalent must be double that indicated by the formula. The amount of carbon to that of nitrogen in the ammonia compound being in the ratio of 8 : 1. The ammoniacal compound is very little soluble in water, and thus affords a ready means of separating this substance from the other products of distillation. On mixing dilute ammonia with the distillate, a milky liquid results, which in a short time deposits sharp rhombic octohedral crystals, and then becomes clear. The crystals are soluble in alcohol and ether, from which they may be again separated by evaporation in a tabular form; when once dried, they are apparently inalterable in the air, but in the moist state or in contact with moist air, they are transformed into a brown mass, and acquire an empyreumatic smell. Slowly heated, the crystals melt and volatilize in the form of drops of liquid, which drops solidify on cooling; rapidly heated they are decomposed, and the smell of ammonia becomes perceptible. Potash evolves no ammonia from the crystals in the cold, and acids separate the original body unchanged. Analysis yielded numbers corresponding to the formula  $C_8H_{21}NO_{12}$ , which, from the numerous analogies which this body presents with ammonia-aldehyde, is viewed as the ammonia compound of butyric aldehyde with water of crystallization, and is then represented by the rational formula  $C_8H_7O \cdot HO + NH_3 + 10 Aq.$  The composition of the liquid body itself thus corresponds with the rational formula  $C_8H_7O \cdot HO$ , which represents butyric aldehyde, and this view of its constitution is verified by the actual production of butyric acid from it, by the oxygen of the air, or from oxide of silver. Compared with butyral, obtained by Chancel by the distillation of butyrate of lime, and which has the same composition, a great resemblance may be observed in the properties of the two bodies, but the boiling points vary, and butyral does not combine with ammonia, nor has butyric acid yet been directly prepared from it by oxidation. The author observed that sulphuretted hydrogen, passed through an alcoholic solution of the ammoniacal compound, gave rise to a disagreeable

empyreumatic odour resembling that of thialdine, and that ether dissolved from the product an oily body containing sulphur, which produced a crystalline substance with hydrochloric acid.

The last product (iv), distilled over an open fire, was heavier than water, it smelt like oil of bitter almonds, and became solid when exposed to the air. It was purified by distillation from chloride of calcium, and proved to be pure oil of bitter almonds. The solid substance into which it is converted by exposure is benzoic acid.

*b. Acid products.*—The concentrated solution containing the acid products, which had been neutralized with chalk, was treated with carbonate of soda and the filtrate from the precipitate of carbonate of lime was evaporated in a water-bath to the consistence of syrup, when a large crop of crystals separated on cooling, which were found to consist of acetate of soda. Further concentration of the mother liquor yielded an additional crop of crystals of the same salt, mixed with other tabular crystals, which could not be separated by water. Alcohol, however, left the latter undissolved, and analysis proved them to be formiate of soda. On re-dissolving this salt in water, and evaporating at the ordinary temperature of the room, it was observed that a salt of formic acid with soda, containing 6 equivs. of water of crystallization was deposited, in the form of fine silky needles, which deliquesced in the air, and effloresced over sulphuric acid. Ordinary formiate of soda has only 2 equivs. of water. The residue after the separation of the acetate and formiate of soda no longer deposited crystals, and it was treated with twice its weight of sulphuric acid diluted with 2 parts of water. Above the crystals of sulphate of soda, which separated after the mixture had remained at rest for a day, was a layer of an aqueous liquid, and upon this floated a brown coloured oil. The latter was carefully removed with a pipette, and washed several times with an equal volume of water to separate the more soluble butyric from valerianic acid, the presence of which in the mixture was indicated by the smell. The water in which the oil had been washed was mixed with the aqueous liquid, and the whole was then saturated with carbonate of soda, and evaporated to dryness in a water-bath. The dry saline mass, treated with sulphuric acid of the above-named strength, yielded a layer of nearly colourless oil, which commenced boiling at a few degrees above 100° C. (212° F.), but no stability was observed in the boiling point until the thermometer indicated 130° C. (266° F.). The liquid which passed over between that temperature and 140° C. (284° F.) was collected apart, and lastly, a small quantity of an acid was obtained that boiled between 160° and 165° C. (310°—329° F.).

The distillate collected between 130° and 140° C. (266° and 284° F.), might, from its smell, have been mistaken for acetic acid, it was soluble in water, although not in all proportions; neutralized with ammonia, it produced a crystalline precipitate with nitrate of silver, which dissolved in boiling water, the greater portion, however, undergoing decomposition.

A crystalline salt was deposited on cooling the aqueous solution, and this was but slightly affected by light; exposed to the heat of a water-bath, however, the crystals became blackened, and fused at a higher temperature with the evolution of acid vapours. The determination of the amount of silver in this compound, and the fact that the salt affords a double compound with acetate of silver, together with the analysis of this double compound, leave no doubt that the acid in question is the metacетonic acid discovered by Gottlieb, the composition of which is expressed by the formula  $C_6H_6O_3$ . The silver salt has the formula  $C_6H_6O_3 \cdot AgO$ , and the double salt with acetate of silver the formula  $C_4H_8O_3 \cdot AgO + C_6H_6O_3 \cdot AgO$ .

The analysis of the last portion of acid, obtained at a temperature between  $160^\circ$  and  $165^\circ$  C. ( $310^\circ$ — $329^\circ$  F.), and that of its silver salt, proved the identity of this product with butyric acid,  $C_3H_7O_2 \cdot HO$ .

The brown-coloured, oily acid separated by the pipette from the aqueous solution of the above acids, and which smelt of valerianic acid, was also distilled; a nearly colourless liquid passed into the receiver, possessing the nauseous smell of the volatile acids of fat, and towards the end of the process a white crystalline sublimate was observed, which, when dissolved out with ether after the last portions had been carbonized in the retort, proved to be benzoic acid.

The colourless, oily distillate was mixed with the residue after the separation of the metacетonic and butyric acids, and saturated with hydrate of barytes. The neutral solution, evaporated over sulphuric acid, yielded salts of three different acids. The least soluble of these was caproate of barytes, the second valerianate of barytes, and the most soluble was butyrate of barytes; there were also indications of the presence of a fourth salt, which, however, could not be more minutely examined.

*II. Products of the action of chromic acid upon casein.*—One part of casein was distilled with 2 parts of bichromate of potash, 3 parts of sulphuric acid, and 30 parts of water. The product in this case had a powerful smell of hydrocyanic acid, which was not entirely removed by agitating the distillate with oxide of mercury. No trace of aldehyde could be found amongst the products. After the removal of the hydrocyanic acid by oxide of mercury, the liquid was neutralized with chalk and again rectified, a turbid aqueous solution was at last obtained, upon which a layer of colourless oil floated; the aqueous liquid afforded on re-distillation an additional quantity of the colourless oil, and with it the last relics of the smell of hydrocyanic acid disappeared. The small quantity of residual fluid was milky, and deposited in the cold a colourless oil, which had a powerful smell of oil of cinnamon, and a burning aromatic taste.

*a. Oily, non-acid products.*—The heavy oil could not be obtained in sufficient quantity for minute investigation, it appears to be somewhat heavier than oil of bitter almonds, does not become solid on exposure to the air, and cannot be distinguished by the smell or taste from oil of cinnamon.

The light, oily liquid afforded two substances, the one of which contained no nitrogen, and was found identical with that produced by oxidation with manganese, and has been represented by the formula,  $C_6H_6O_2$ . The other, containing nitrogen, passed over at a temperature between  $120^\circ$  and  $140^\circ$  C. ( $248^\circ$ — $284^\circ$  F.), and by rejecting, on re-distillation, the first and last portions, acquired a steady boiling point between  $125^\circ$  and  $128^\circ$  C. ( $257^\circ$ — $263^\circ$  F.), its specific gravity was 0.813 at  $+15^\circ$  C. ( $59^\circ$  F.), its smell resembled that of oil of bitter almonds, its taste was bitter, aromatic, and burning; it was perfectly colourless, mobile, soluble in about four times its weight of water, miscible in all proportions with alcohol and ether, and burnt with a white flame without smoke. When heated with a solution of potash, this substance evolved ammonia, and the alkaline liquid then saturated with sulphuric acid, threw up globules of oil, which, when re-distilled, exhibited a strong acid reaction, and possessed a smell resembling that of valerianic acid. All these properties indicated a striking similarity between this substance and the valeronitrile discovered by Schlieper among the products of the oxidation of gelatine by chromic acid. The analysis of the body, and the determination of the specific gravity of its vapour, established its identity with valeronitrile, and this identity was still further confirmed by the direct production of valerianic acid from it by the action of acids. The formula for valeronitrile is  $C_{10}H_9N$ .

The fluid residue in the retort after the separation of valeronitrile, which boiled at a temperature above  $128^\circ$  C. ( $263^\circ$  F.), was evaporated, and left a very small quantity of a substance that had no smell of cinnamon, but became solid on exposure to the air. This, from its physical properties, was recognized as benzoic acid, and indicated the presence of oil of bitter almonds amongst the products of oxidation.

The valeracetonitrile of Schlieper could not be detected in the liquid, which distilled over between the temperatures of  $68^\circ$  and  $70^\circ$  C. ( $155^\circ$ — $158^\circ$  F.), although its existence appeared probable.

*b. Acids.*—Hydrocyanic acid has already been noticed as one of the chief products of this process of oxidation, and in removing this acid by oxide of mercury, the reduction of a small quantity of the latter indicated the presence of formic acid. The other acids were detected nearly in the manner already described in the former process, when manganese was employed. Benzoic acid was found in considerable quantity, also acetic, valerianic, and butyric acids. The valerianic acid was contaminated with a small quantity of an acid with a higher equivalent, and there were symptoms of the presence of metacetonic acid with the butyric, which, however, could not be decidedly proved.

The series of products obtained by the oxidation of casein with these two different agents, are arranged in the following order for the sake of easy comparison :—

With peroxide of manganese.

Aldehyde of acetic acid . . . C<sub>4</sub>H<sub>3</sub>O, HO

" " metacetonic acid? C<sub>6</sub>H<sub>5</sub>O, HO

" " butyric acid . . . C<sub>8</sub>H<sub>7</sub>O, HO

Oil of bitter almonds . . . C<sub>14</sub>H<sub>5</sub>O<sub>2</sub>, H

Formic acid . . . . . C<sub>2</sub>H O<sub>3</sub>, HO

Acetic acid . . . . . C<sub>4</sub>H<sub>3</sub>O<sub>3</sub>, HO

Metacetonic acid . . . . . C<sub>6</sub>H<sub>5</sub>O<sub>3</sub>, HO

Butyric acid . . . . . C<sub>8</sub>H<sub>7</sub>O<sub>3</sub>, HO

Valerianic acid . . . . . C<sub>10</sub>H<sub>9</sub>O<sub>3</sub>, HO

Caproic acid . . . . . C<sub>12</sub>H<sub>11</sub>O<sub>3</sub>, HO

Benzoic acid . . . . . C<sub>14</sub>H<sub>5</sub>O<sub>3</sub>, HO

With chromic acid.

Aldehyde of metacetonic acid? . . . . . C<sub>6</sub>H<sub>5</sub>O, HO

Oil of bitter almonds . . . C<sub>14</sub>H<sub>5</sub>O<sub>2</sub>, H small quantity.

Formic acid . . . . . C<sub>2</sub>H O<sub>3</sub>, HO small quantity.

Acetic acid . . . . . C<sub>4</sub>H<sub>3</sub>O<sub>3</sub>, HO

Metacetonic acid . . . . . ?

Butyric acid . . . . . C<sub>8</sub>H<sub>7</sub>O<sub>3</sub>, HO

Valerianic acid . . . . . C<sub>10</sub>H<sub>9</sub>O<sub>3</sub>, HO small quantity.

Benzoic acid with traces of caproic acid . . . . . ?

Benzoic acid . . . . . C<sub>14</sub>H<sub>5</sub>O<sub>3</sub>, HO

Hydrocyanic acid . . . . . C<sub>2</sub>NH

Valeronitrile . . . . . C<sub>10</sub>H<sub>9</sub>N

Heavy oil with the odour of oil of cinnamon . . . . . ?

Hydrocyanic acid and valeronitrile may be viewed as the ammonia salts of formic and valerianic acids, from which the elements of 3 equivs. of water have separated by the action of a high temperature. The apparent discrepancy in the nature of the products from the two agents employed is thus explained, and the reaction observed with alkalies upon the residuum of distillation fully bears out this view of the subject.

When the residue from the distillation of casein with peroxide of manganese and sulphuric acid is saturated with lime, ammonia is evolved in such quantity as might lead to the supposition, that the whole of the nitrogen in the casein is retained as ammonia in combination with sulphuric acid. The residue from the distillation with bichromate of potash and sulphuric acid, on the other hand, evolves hardly a trace of ammonia when saturated with lime.

In the former process, the sulphuric acid was so proportioned to the peroxide of manganese, that about  $\frac{1}{4}$  of the acid would remain free in the liquid, and if the action of sulphuric acid and oxygen upon casein is of such a character as to give rise to the formation of valerianate and formate of ammonia, the ammonia would necessarily remain in combination with the sulphuric acid, and the acids would distil over.

The proportion of sulphuric acid to that of bichromate of potash in the latter process was such as would just about suffice to saturate the potash and oxide of chromium. Valerianic and formic acids could, therefore, under these circumstances combine with ammonia, and these acids would only be found in the distillate, when the ammonia present was insufficient to saturate them, or when the sulphuric acid was in excess. It was remarked by Schlieper, in acting upon gelatine, and confirmed by the author with casein, that valeronitrile and hydrocyanic acid were only obtained when no excess of sulphuric acid had been used in the process.

The observation of Döbereiner, that formiate of ammonia is converted into hydrocyanic acid and water at a temperature of  $180^{\circ}$  C. ( $356^{\circ}$  F.), and Fehling's experiment, in which benzoate of ammonia is converted into benzonitrile and water at a high temperature, are conclusive evidence as regards the production of hydrocyanic acid and valeronitrile from the formiate and valerianate of ammonia respectively. The temperature employed in the decomposition with sulphuric acid and bichromate of potash was sufficiently high to effect this change, and it would therefore appear, that the production of valeronitrile and hydrocyanic acid is due to the relation between the quantities of sulphuric acid and bichromate of potash aided by a high temperature, and not to the nature of the oxidizing agents.

The proportions of peroxide of manganese and bichromate of potash used in the experiments with an equal weight of casein, were such as would afford a nearly equal amount of oxygen, but the results of the action prove, that there was an excess in the case of the bichromate, or the aldehydes of acetic and butyric acids would also have been found amongst the products. It is not likely that valeronitrile will be obtained when manganese is employed as an oxidizing agent, for its use implies the presence of an excess of sulphuric acid.

Gelatine, fibrin, and albumen were also treated with peroxide of manganese and sulphuric acid, in the manner already described for casein, and all yielded aldehyde. In the case of gelatine, the body  $C_6H_6O_2$  (aldehyde of metacetoic acid?) was not obtained, and only small quantities of it were discovered in the products from fibrin and albumen. The aldehyde of butyric acid was produced in greatest quantity from fibrin, and a comparatively small quantity only from the other two substances. All the three bodies yielded large quantities of acetic and formic acids. Fibrin afforded the most butyric, and gelatine the most valerianic acid. All three yielded small quantities of benzoic acid. From fibrin, metacetoic acid was distinctly produced. The presence of caproic acid in the products of distillation was rendered highly probable by the sweaty odour of the valerianic acid, and by the slight excess of silver obtained in the analysis of the salts of that acid.

The same bodies treated with chromic acid, afforded the same products as were obtained by acting upon casein; much hydrocyanic acid was generated, and also the peculiar oil, smelling like oil of cinnamon, although in small quantity. The benzoic and acetic acids were the most abundant acid products. Fibrin yielded more butyric acid than albumen or even than casein.

This most elaborate series of experiments establishes the important fact that the products of oxidation of the bodies in question are constant, and not dependant upon the nature of the oxidizing agent. A certain amount of oxygen is the only indispensable condition to the completion of this interchange of the elements; and it appears to be without influence upon the nature of the products, whether the oxygen is afforded them in a shorter

or longer space of time. It is not assumed that the bodies enumerated are the direct products of oxidation of casein, fibrin, &c., but they result, no doubt, from the action of oxygen upon certain groups of atoms, which are supposed to form the proximate constituents of this whole class of substances.

If the four substances under examination are compared with reference to the amount of nitrogen which they respectively contain, fibrin appears as an intermediate or transition member of the series, in passing from casein and albumen on the one hand, to gelatine on the other.

If the respective quantities of acetic acid and aldehyde yielded by oxidation are made the point of comparison, beginning with those which afford the least, casein and albumen again take the lead, fibrin intervenes, and gelatine affords those products in greatest quantity. Formic acid was also obtained most abundantly from gelatine; and it would therefore appear as if aldehyde, acetic and formic acids were derivatives of the same group of atoms. The order of the series is reversed when the quantities of benzoic acid and oil of bitter almonds produced from these substances are compared. They then range in the following order: gelatine, albumen, fibrin, casein. Fibrin is singular as the source of the largest quantity of butyric acid, and this was obtained in minimum from gelatine. Gelatine, on the contrary, yielded the largest proportion of valerianic acid, and casein and albumen the least. Thus, in three cases, fibrin, assumes a position intermediate between casein and albumen on the one side, and gelatine on the other; and it only alters its relative position when viewed with reference to the amount of butyric acid, which was obtained from it in the largest proportion.

The production of aldehyde from the constituents of the blood, casein and gelatine, render it probable, in the author's opinion, that this body should also be obtained by the restricted oxidation of fat; and the probability is strengthened by the fact that aldehyde is actually produced when milk-sugar is distilled with bichromate of potash and sulphuric acid, and also, (as recorded in an experiment of Engelhardt), by the dry distillation of lactate of copper.

Bearing this in mind, there appears ground for assuming some non-nitrogenous group of elements as one of the proximate constituents of the bodies under examination (*e. g.* milk-sugar, or fat), and that this, under the influence of oxygen, gives rise to aldehyde.

Further, when the production of albumen, fibrin, and gelatine is constantly observed during the growth of a young animal from milk-sugar, casein, some fat and inorganic substances, which constitute the whole of its food, we are almost led to believe that these bodies must be derived from casein, by the addition of the elements of milk-sugar; or as this does not enter into the composition of blood, by the addition of fat or lactic acid, into which milk-sugar is easily convertible. Judging from the quantities of aldehyde obtained from the four substances, albumen would be the first product from casein, fibrin would then follow, and the last

would be gelatine. It is not supposed that these substances are the direct product of the union of casein with fat, &c., as in that case the amount of nitrogen in fibrin must be less than in albumen or casein, and this is not the fact. But, again, this may be explained by the assumption that, on the addition of the elements of fat to those of casein, another group of elements, and that group, namely, which gives rise to the formation of benzoic acid and oil of bitter almonds, simultaneously separates from combination. Casein afforded, as stated above, the largest proportion of oil of bitter almonds, and gelatine, the least. The uniformity in the proportions of carbon and hydrogen in casein, albumen, and fibrin, and their slight variation in gelatine, would thus be accounted for, and at the same time, the large amount of nitrogen in fibrin and gelatine.

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*Chemical Examination of the Bile of the Ox.\**—The account of an elaborate investigation of the bile of the pig was published a short time since by Drs. Strecker and Grundelach, in which the chief ingredient of that secretion was represented as the soda salt of a new acid, termed by the authors, hyocholinic acid. Dr. Strecker has since extended his researches to the bile of the ox, and has arrived at very different conclusions respecting its nature to those deduced from the experiments of former analysts.

The first experiments were made with ox-bile, purified and crystallized in the manner described by Platner, and subsequently by Verdeil; but notwithstanding the great uniformity in the amounts of carbon, hydrogen, and sulphur obtained from different analyses, the substance when examined under the microscope, was found to consist obviously of a mixture of crystals with an amorphous body, and all further analytical investigation of it was consequently abandoned. The same crystallized bile, which still contained traces of alcohol and ether, was then treated with water and sulphuric acid, until the latter produced a slight turbidity; in the course of a few hours, needles grouped in a stellar-form appeared, and continued to increase in quantity until after twelve hours the whole fluid was intersected by them and converted into a white mass, which when thrown upon a filter and washed with cold water, was very much diminished in bulk. These crystals were boiled in water, when the greater portion dissolved and was again deposited on cooling. The soluble portion possessed all the properties of Gmelin's cholic acid; 1000 parts of cold water dissolved 3·3 parts of the acid, and 8·3 parts were taken up by the same quantity of boiling water. Under the microscope, the crystals appear to consist of exceedingly minute needles, which dry up on the sides of the paper filter and line it with a thin silky layer. The cold aqueous solution has a sweet and somewhat bitter taste, reddens litmus-paper, and exhibits no reaction with acids, with acetate of lead, with bichloride of mercury, or with nitrate of silver; basic acetate of lead produces a slight precipitate with the acid.

The acid is very soluble in alcohol, which when evaporated from a water-

\* *Ann. der Chem. und Pharm.*, lxxv, p. 1.

bath, leaves it as a syrupy or resinous mass, and this, as was observed by Platner, cannot be re-converted entirely into the crystalline form. Spontaneous evaporation of the alcohol from a watch-glass leaves the acid in the form of resinous rings, which are converted by a few drops of water into groups of needles; when water is added to the alcoholic solution until a troubled appearance is produced, and the mixture is allowed to stand, annular crystals appear in the course of twelve hours, and the liquid becomes perfectly clear. The acid is very little soluble in ether, but a considerable quantity of ether is required to precipitate it from an alcoholic solution. Ether containing a little alcohol dissolves it more freely, and crystals are formed by the spontaneous evaporation of the solvent. Concentrated cold sulphuric acid dissolves the acid readily, as do also hydrochloric and acetic acids, and from the latter it can again be obtained in crystals.

The solutions of cholic acid in concentrated mineral acids are rendered turbid by heat, and oily drops quickly subside. Aqueous solutions of ammonia, potash, and soda dissolve cholic acid in large quantity, as does also water of barytes. On the addition of acids to these solutions, a resinous precipitate is formed, which resolves itself, on standing, into crystals, resembling wavellite in form. Ether facilitates this assumption of the crystalline form. The neutral salts of the acid exhibit the following reactions with salts of the metallic oxides. Lime, barytes, strontian, and magnesia cause no precipitate in the aqueous solution of the acid; a flocculent precipitate is caused by acetate of lead, and subsequently a fresh precipitate is produced by the basic acetate, but in very much less abundance. The fluid filtered from the latter contains a little oleic acid. Salts of copper produce blueish-white, and the chlorides of iron, yellow flakes in the solution, which are readily soluble in alcohol; nitrate of silver produces a voluminous gelatinous precipitate, in a solution containing 1 per cent of cholic acid, which is partially dissolved by heating the liquid, and is again deposited in the cold. A slow process of cooling separates the salt in crystalline needles; a more rapid process causes it to subside in the gelatinous form, which, however, is rendered crystalline by a few drops of ether. The precipitate becomes blackened by exposure to light, but little or not at all in the dark, even when boiled. All the salts of cholic acid are soluble in alcohol.

The substance that remained insoluble in boiling water, exhibited under the microscope crystalline laminae, with a lustre of mother-of-pearl, some of which were perfect six-sided tables. With the exception of their insolubility and crystalline form, no difference could be observed in the physical or chemical properties of this body from cholic acid; and indeed, when dissolved in alcohol and the solution treated subsequently with water, needle-like crystals of cholic acid separated. The author consequently considers this substance as a modification of cholic acid, and assigns it the name of Paracholic acid. The salts of the two acids exhibit no reactions calculated to establish a distinction between them. Both

acids exhibit with sugar and sulphuric acid Pettenkofer's test for bile in a very marked manner, and Dr. Strecker finds that acetic acid may be conveniently substituted for sugar in that reaction.

It was still necessary to show that these acids were not products of decomposition caused by the process of evaporation or by the sulphuric acid used in preparing them, and for this purpose the bile, fresh from the gall-bladder, was precipitated with neutral acetate of lead; the precipitate was washed with cold water, dissolved in a small quantity of boiling alcohol, and sulphuretted hydrogen passed through the solution; the alcoholic solution from the sulphuret of lead was mixed with a large quantity of water previously used in washing the precipitate, and when it began to pass milky through the filter, the mixture was set aside, and at the expiration of twelve hours, a crystalline mass was obtained, consisting of the two modifications of the acid, which could be separated in the manner already indicated. The author obtained in this manner 13·5 grms. (208.5 grains) of cholic and paracholic acids from the contents of ten gall-bladders. This latter process is preferable, as absolute alcohol and ether are dispensed with in the preparation of the acids. It thus appears that cholic acid is contained ready formed in the bile, and is chiefly contained in the precipitate produced by neutral acetate of lead. The precipitate subsequently obtained with basic acetate, however, also yielded a small quantity of cholic acid. The analysis of these acids and the atomic weight deduced from the soda and barytes salts led to the following composition in 100 parts:

	Equivs.	Calculated.	Mean of experiments
Carbon . . . . .	52	312	67·10
Hydrogen . . . . .	43	43	9·25
Nitrogen . . . . .	1	14	3·01
Oxygen . . . . .	12	96	20·64
		465	100·
			100·

The formula for the acid is consequently  $C_{52}H_{43}N O_{12}$ , whilst that contained in the salts is represented by  $C_{52}H_{42}N O_{11}$ .

Dr. Strecker prepared and analyzed cholate of soda, which perfectly resembles crystallized bile in appearance; it is, however, very difficultly obtained in a crystalline form. The analysis of this salt yielded:

	Calculated.	Mean of experiments.
C 52	312	64·06
H 42	42	8·62
N 1	14	2·87
O 11	88	18·09
Na O 1	31	6·36
		6·17

The amounts of carbon and hydrogen in this salt are considerably higher than those found by Theyer and Schlosser in purified bile, the mean of their experiments yielding 57·7 per cent carbon, and 8·3 per cent hydro-

gen, although the amounts of nitrogen and soda in both substances nearly coincided. There must consequently be another substance associated with cholate of soda in bile, containing the whole of the sulphur, more carbon and hydrogen than the cholate, and which yields with acids a resin, taurine, and ammonia. This is no doubt choleate of soda.

Cholate of ammonia ( $C_{52} H_{42} NO_{11}, NH_4O$ ) is prepared by passing dry ammoniacal gas into an alcoholic solution of cholic acid, as long as crystalline needles are formed. Cholate of barytes ( $C_{52} H_{42} N_{11}, BaO$ ) is an amorphous substance, obtained by evaporating a solution of cholic acid in water of barytes, after the removal of the excess of barytes by carbonic acid.

An account of the products of decomposition of cholic acid is promised by the author as the subject of a future paper; and it is merely stated at present, that when cholic acid is boiled with concentrated acids, it appears to yield nitrogenous acids with the loss of successive atoms of water. If ebullition is kept up for a length of time with hydrochloric acid, the residue becomes insoluble in alcohol. Concentrated alkali gradually eliminates ammonia and a carbonaceous matter, whilst a non-nitrogenous acid remains, identical in composition with the cholic acid of Demarçay, and which is called cholalic acid by the author.

Dr. Strecker concludes the present investigation by stating the details of two experiments, instituted for the purpose of ascertaining the quantity of the bilin of Berzelius contained in bile. The result yielded 2 per cent of bilin in dry bile, which is conclusive evidence that this substance is not the chief ingredient of bile. The bilin obtained in the manner prescribed by Berzelius, left an ash on incineration; and it is the author's opinion, that if the mode of separating the whole of the bases in the preparation of bilin were absolutely accurate, not a trace of this substance would be obtained. That portion of the bile which is not precipitated by salts of lead (the bilin of Berzelius), has been stated by Theyer and Schlosser to possess the same composition as the bile itself, and Dr. Strecker has confirmed the opinion of the latter chemists.

The bile cannot, therefore, be constituted of two distinct substances; the one of which is precipitated by salts of lead, and the other not. On the contrary, the precipitate, with neutral acetate of lead, has been shown to be a lead-salt of an acid, containing nitrogen but no sulphur, whilst that produced by basic acetate of lead contains a portion of the former mixed with an acid containing sulphur, and the bile is thus shown to be a mixture of the soda salts of these acids.

If the presence of these two acids ready formed in the bile is admitted, all the phenomena described with reference to this secretion are easily explained. The choleic acid containing sulphur is not precipitated by acids, and its presence impedes the precipitation of cholic acid by weak or even by strong acids. But in the presence of much cholic acid, some choleic is also precipitated by acids, as the precipitate contains sulphur, although in variable proportions, and the tendency which these two acids

exhibit to accompany each other in all cases has been erroneously considered a ground for supposing them to be in conjugate combination, although it is much more probable that the precipitates containing both acids are mere mechanical mixtures. The author opposes the view of Berzelius and Mulder, that the acids of the bile are conjugate compounds of the acids with bilin, by proving, from Mulder's analysis, that the proportion of bilin in the salts of bilifellinic acid is never constant, and that simple treatment with ether is sufficient to separate the supposed conjuncts. Additional evidence in favour of the acid character of the constituent containing the sulphur in bile is afforded by the same experiments of Mulder, which show that the saturating power of the fellinic and cholinic acids is rather increased than diminished by the assumption of the bilin as a conjunct, whilst all experience tends to prove that the saturating power of an acid is diminished when a conjunct enters into combination with it, unless the conjunct itself possess an acid character; and even in that case, the saturating power is not always augmented.

It appears, therefore, that the bile of all animals contains a mixture of a nitrogenized acid freed from sulphur, and an acid comprising both sulphur and nitrogen amongst its elements, both of which are chiefly in combination with soda. That the relative quantity of both substances is pretty much the same in the same class of animals, as is evinced by the uniform results obtained from the bile of the ox, but varies exceedingly in different classes of animals; this is proved by the variable quantities of sulphur obtained from the bile of different animals. In the bile of the serpent (*boa anaconda*) 6·3 per cent\* of sulphur was discovered, whilst little or none was found in that of the pig. The substance containing the sulphur of the bile is probably the same in all cases (pig's bile excepted) as taurine can always be obtained from it. A difference, however, is observed in the nature of the other constituents of pig's and ox-bile, which are the only two that have yet been carefully examined.

The acid of pig's bile (hyocholinic acid) is expressed by the formula  $C_{54} H_{43} N O_{10}$ , that of ox-bile (cholic acid)  $C_{52} H_{43} N O_{12}$ . If two atoms of water are deducted from the elements of the latter formula, there remain:  $C_{52} H_{41} N O_{10}$ , which formula differs from that expressing the composition of hyocholinic acid by  $C_2 H_2$ , or by the elements of the carbo-hydrogen, which constitute the distinction between the volatile fatty acids having the formula  $(CH)_n O_4$ . These two atoms of water are, in fact, separated on boiling cholic acid with hydrochloric acid, and the resulting resinous body exhibits great similarity to hyocholinic acid.

\* Ann. der Chem. und Pharm. Lx. 109.

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IX. *Analysis of the Water of the Artesian Wells, Trafalgar Square,*  
*By F. A. ABEL and THOS. H. ROWNEY, ESQRS., Assistants at the*  
*Royal College of Chemistry.*

The deep well-water of the London Basin has been analysed by Professor Graham.\* The striking feature of this analysis is the discovery of the presence of phosphoric acid, and the absence of salts of potash.

The water which Professor Graham analysed, was taken from the deep well in the brewery of Messrs. Combe and Delafield, Long Acre. This well not descending so deep into the chalk as the Artesian wells in Trafalgar Square, we were induced to subject the water of the latter to an analysis in order to compare the results with those obtained by Professor Graham. The water on which we operated was taken in the beginning of October, 1847, from the shaft at the back of the National Gallery.

At a depth of about 109 feet, the water enters the shaft through a bore-hole, which passes the London clay and penetrates into the chalk. Thus the water rises from a depth of nearly 400 feet. The temperature of the water is 58° Fahr. (14·5° C.), its sp. gr. is 1000·95, the sp. gr. of distilled water being 1000.

The water is very soft, and very delicate test-papers show that it has an alkaline re-action.

\* Memoirs of the Chemical Society, vol. II. p. 239.

A careful qualitative analysis of the water having pointed out the presence of potash, soda, magnesia, lime, sulphuric, silicic, carbonic, hydrochloric acids, and traces of phosphoric acid, as well as a small quantity of organic matter and ammonia, the following experimental numbers were obtained by quantitative analysis.

**A. Determination of the total amount of fixed constituents :**

Amount of water.	Fixed residue.	Per centage.
I. 1097,895 grms.	1,0929 grms.	0,09954
II. 1009,028 ,	0,9965 ,	0,09876
		<i>Mean</i> 0,09915

**B. Determination of sulphuric acid :**

Amount of water.	Amount of sulphate of baryta.	Per centage of sulph. acid
I. 356,464 grms.	0,1657 grms.	0,01598
II. 326,303 ,	0,1527 ,	0,01607
		<i>Mean</i> 0,016025

**C. Determination of chlorine :**

Amount of water.	Amount of chloride of silver.	Per centage of chlorine.
I. 208,481 grms.	0,1465 grms.	0,01738
II. 339,337 ,	0,2390 ,	0,01741
		<i>Mean</i> 0,017395

**D. Determination of silicic acid :**

Amount of water.	Amount of silicic acid.	Per centage.
I. 547,155 grms.	0,0073 grms.	0,00133
II. 516,700 ,	0,0067 ,	0,00129
		<i>Mean</i> 0,00131

**E. Determination of lime :**

Amount of water.	Amount of carbonate of lime.	Per centage of lime.
I. 547,155 grms.	0,0255 grms.	0,00261
II. 516,700 ,	0,0242 ,	0,00262
		<i>Mean</i> 0,002615

**F. Determination of magnesia :**

Amount of water.	Amount of pyrophosphate of magnesia.	Per centage of magnesia.
I. 547,155 grms.	0,0237 grms.	0,00159
II. 516,700 ,	0,0217 ,	0,00153
		<i>Mean</i> 0,00156

## G. Determination of the alkalies :

Amount of water.	Amount of chlorides of potassium and sodium.	Per centage.
I. 245,307 grms.	0,2015 grms.	0,08206
II. 219,182 ,,	0,1920 ,,	0,08759
Amount of water.	Amount of potassiochloride of platinum.	Per centage of potash.
I. 245,307 grms.	0,1277 ,,	0,01008
II. 219,182 ,,	0,1255 ,,	0,01101
<i>Mean</i>		<b>0,01055</b>
Amount of water.	Amount of chloride of sodium.	Per centage of soda.
I. 245,307 grms.	0,16255 grms.	0,03467
II. 219,182 ,,	0,15380 ,,	0,03713
<i>Mean</i>		<b>0,03590</b>

## H. Determination of carbonic acid :

The carbonic acid was determined by precipitating a known volume of water by a mixture of chloride of calcium and ammonia at the well. 2134,0254 cubic centimetres of water in this manner yielded 1,3397 grms. of precipitate, in which the carbonic acid was determined.

Amount of precipitate.	Amount of carbonic acid.	Per centage in the precipitate.
I. 0,3656 grms.	0,117 grms.	32,002
II. 0,3679 ,,	0,118 ,,	32,070
<i>Mean</i>		<b>32,036</b>

The whole amount of precipitate accordingly contained 0,4297 grms. carbonic acid, representing a per centage of 0,02013 carbonic acid in the water.

## I. Determination of the total amount of phosphoric acid :

A known quantity of water was evaporated to dryness, the residue obtained was fused in a platinum capsule, the fused mass digested with water, the solution filtered, and the phosphoric acid determined therein as pyrophosphate of magnesia.

Amount of water.	Amount of pyrophosphate of magnesia.	Per centage of phosphoric acid in the water.
1002,208 grms.	0,0037 grm.	0,000233

For the determination of the small amounts of phosphoric acid, in combination with lime, of organic matter existing in the water in

the different forms designated as apocrenic and crenic acids, and of extractive matter,

36,31712 kilogrammes of the water were evaporated to 306,923 grms. yielding a precipitate (*a*), insoluble in water, of . . . 2,899 „  
the solution (*b*) along with the washings amounting to 569,306 „

**K. Determination of the phosphoric acid in combination with lime :**

Amount of precipitate ( <i>a</i> ). 0,6925 grm.	Amount of pyrophosphate of magnesia. 0,0032 gm.	Per centage of phosphoric acid in the water, combined with lime. 0,0000234
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**L. Determination of the organic matter :**

0,6100 grm. of precipitate (*a*) was extracted with potash, the alkali was saturated with acetic acid, and acetate of copper added; there was obtained, after standing for some time,

0,0189 grm. of a brown precipitate of apocrenate of copper, corresponding to 0,0001414 per cent of apocrenic acid in the water.

The filtrate from this precipitate, on boiling with excess of carbonate of ammonia, yielded:

0,0567 grm. of a greenish precipitate of crenate of copper, corresponding to 0,000196 per cent of crenic acid in the water.

For the determination of what is usually called extractive matter: 189,50 grms. of the solution (*b*) were evaporated with carbonate of soda, the residue obtained was dried, weighed and afterwards ignited; it lost 0,1165 grm. corresponding to :

0,00096 per cent of extractive matter in the water.

From these analytical results, the following composition of the water is deduced :

	Grammes in 100 kilogrammes. (liter).	Grains in an imperial gallon. (70,000 grs.)
Carbonate of lime . . .	4,65000 . . .	3,255000
Phosphate of lime . . .	0,04863 . . .	0,034041
Carbonate of magnesia . .	3,22000 . . .	2,254000
Sulphate of potash . . .	19,53000 . . .	13,671000
Sulphate of soda . . .	12,49900 . . .	8,749300
Chloride of sodium . . .	28,65500 . . .	20,058500
Phosphate of soda . . .	0,41600 . . .	0,291000
Carbonate of soda . . .	25,78400 . . .	18,048800
Silicic acid . . . . .	1,31000 . . .	0,971000
Apocrenic acid . . . .	0,14100 . . .	0,098700
Crenic acid . . . .	0,19600 . . .	0,137200
Extractive matter . . .	0,96000 . . .	0,672000
	97,40963	68,240541

The amount of fixed residue obtained by direct experiment was :

in 100 kilogrammes . . . .	99,150 grammes ;
in an imperial gallon . . . .	69,405 grains.

According to the experiments detailed above, one liter of water contains 30,3864 cubic centimetres of free carbonic acid at the temperature 58,1° F. (14,5° C.) ; one imperial gallon contains, therefore, 8,4235 cubic inches.

In order to ascertain whether the water loses a portion of carbonic acid in being pumped up, a determination of this gas was made in some of the water, as it issued from the mouth of the force-pump in the works :

Water employed.	Precipitate obtained.	Per centage of carbonic acid in the water.
1067,012 cubic centimeters	0,2103 grm.	0,01971

After deducting the amount of carbonic acid in combination with lime, magnesia, and soda, from the per centage obtained above, we have remaining a quantity corresponding to 28,153 cubic centimeters in a liter, or 7,805 cubic inches in an imperial gallon at 14,5° C.

From these results, it is evident that a small quantity of carbonic acid is lost by the process of pumping.

To ascertain the amount of matter precipitated by boiling the water, known quantities were submitted to strong ebullition for some time, the precipitates formed were collected on tared filters, dried and weighed.

Water employed.	Precipitate formed.	Per centage.
439,608 grms.	0,0392 grm.	0,00892
357,393 ,,	0,0320 ,,	0,00895
<i>Mean</i> 0,008935		

The mean quantity obtained corresponds to 6,2545 grains in an imperial gallon, or 0,08935 grammes in a liter.

The preceding analysis shows that the constituents of the water of the Artesian wells in Trafalgar Square are essentially the same as those of the water from the well in Messrs. Combe and Delafield's brewery. There is only one point in which the two waters materially differ in composition. The water which Professor Graham analysed, and which, as already mentioned, comes from a higher stratum, was found to contain no potash salts, whilst these were invariably present in the waters of Trafalgar Square. In order to preclude the possibility of error, the water which we employed for testing was collected at different periods.

Mr. Payen\* found that the water of the Artesian well at Grenelle contains a considerable amount of sulphate of potash and chloride of potassium, so that it would appear that potash salts are characteristic of the waters from the deeper strata.

The water analysed by us did not contain a trace of iron.

The presence of phosphoric acid, first pointed out by Professor Graham in deep well-water, could be easily ascertained in the Trafalgar Square water by the method indicated by that chemist; in fact, on evaporating the water to dryness, and gently igniting the residue, the phosphoric acid, existing partly in combination with lime and partly with soda, is obtained altogether in the form of a soda salt, the solution of which deposits the yellow tribasic silver-salt on the addition of nitrate of silver.

The large amount of organic matter contained in the deep well-water is very remarkable, while the quantity observed in the water of a higher stratum seems to have been very trifling. It evidently arises from the remains of organized beings which have invariably been found in the chalk.

With reference to the quantities in which the different constituents are present, it will be observed, on comparison, that the total amount of fixed constituents is somewhat different (56,80 and 69,40), whilst very considerable deviations are perceptible in the quantities of the various constituents. The most striking difference is observed in the quantities of sulphate of soda contained in the two waters.

In conclusion, we give a tabular view for the comparison of the water analysed by Professor Graham and the Trafalgar Square water, to which we annex the results obtained by M. Payen from the analysis of the water of Grenelle.

	Wells at Messrs. Combe & Delafield.	Trafalgar Square wells.	Grenelle.
	Grains in an imperial gallon.		
Carbonate of lime . . . . .	6,18	3,255000	4,7600
Phosphate of lime . . . . .	0,19	0,034041	· ·
Perphosphate of iron . . . . .	0,24	· · ·	· ·
Carbonate of magnesia . . . . .	1,08	2,254000	0,9940
Sulphate of potassa . . . . .		13,671000	0,8600
Chloride of potassium . . . . .		· · ·	0,7630
Bicarbonate of potassa . . . . .		· · ·	2,0720
Sulphate of soda . . . . .	24,25	8,749300	· ·
Chloride of sodium . . . . .	12,74	20,058500	· ·

\* Annales de Chimie et de Physique, 3ème sér. tom. 1. p. 381.

	Wells at Messrs. Combe & Delafield.	Trafalgar Square wells.	Grenelle.
	Grains in an imperial gallon.		
Phosphate of soda . . . . .		0,291000	.
Carbonate of soda . . . . .	11,68	18,048800	.
Silicic acid . . . . .	0,44	0,971000	0,3990
Apocrenic acid . . . . .		0,098700	.
Crenic acid . . . . .		0,137200	.
Extractive matter . . . . .		0,672000	.
Yellow substance . . . . .		.	0,0014
Organic matter (nitrogenous) . . . . .		.	0,0138
	56,80	68,240541	9,8632

The purity of the water of Grenelle is most remarkable, the amount of fixed constituents being only about  $\frac{1}{4}$ th of that which is found in the London waters.

This analysis was conducted in the laboratory of the Royal College of Chemistry.

*On the Composition and Distribution of the Inorganic Substances in the different Organs and component Organic Parts of the Mulberry Tree. By THORNTON JOHN HERAPATH, Esq.*

In all the analyses of plant-ashes that have hitherto been published, either the ash of the entire plant, or of some one or other organ of the plant only has been examined. Now it is well known that all the organs of plants, without exception, are composed of at least three different, and perfectly distinct, parts; viz: cellulose, the various incrusting matters, and the fluid contents of the cells, which occur in very variable proportions, and all of which contain their peculiar inorganic substances. When, therefore, such an ash is analysed, we merely ascertain the composition of the mixed ashes of these different parts; but we do not determine, either the proportion, or composition, of the ashes yielded by each of them individually. As I was well aware of the advantages that would result from such an investigation, I undertook a series of analyses of the inorganic substances contained in the different organs of the common mulberry tree (*Morus nigra*), and likewise of those in each of the separate parts of which those organs are composed, with the view of determining not only their proportion and composition, but also their relation one to another.

I should observe that the mulberry tree which furnished the materials for this investigation, grew on the millstone grit formation.

#### I.—ANALYSES OF THE ASHES OF THE ENTIRE ORGANS.

14449·4 grains of freshly gathered, and partly ripe berries gave 1079·1 grs. of dry vegetable matter, and furnished, upon incineration, 100· grs. of ash.

3999·3 grs. of fresh mulberry leaves gave 979·8 grs. of dry vegetable matter, and furnished 100· grs. of ash upon incineration.

7681·8 grs. of freshly cut branch, gave 3833·3 grs. of dry vegetable matter, and furnished 100· grs. of ash upon incineration.

These ashes were found to have the following per centage composition :

	Berries.	Leaves.	Branch.
<b>SOLUBLE SALTS :</b>			
Carbonic acid . . . . .	19·131	8·937	3·939
Sulphuric acid . . . . .	traces.	10·075	1·530
Phosphoric acid . . . . .	1·219	0·307	traces.
Potash . . . . .	23·655	21·432	} 11·666
Soda . . . . .	13·034	7·060	
Chloride of sodium . . . . .	1·499	1·681	
<b>INSOLUBLE SALTS :</b>			
Carbonate of lime . . . . .	13·412	24·611	56·969
,,    ,, magnesia . . . . .	3·657	1·537	traces.
Sulphate of lime . . . . .	traces.	traces.	traces.
Phosphate of lime . . . . .	21·704	14·356	17·420
,,    ,, magnesia . . . . .	traces.	traces.	traces.
,,    ,, peroxide of iron . . . . .	0·243	0·512	0·765
,,    ,, manganese . . . . .	—	—	traces.
Silicic acid . . . . .	2·438	9·485	6·060
	99·992	99·993	100·000

Or, deducting the carbonic acid, the composition of the real inorganic substances is as follows :

	Berries.	Leaves.	Branch.
<b>SOLUBLE SALTS :</b>			
Sulphuric acid . . . . .	traces.	12·694	2·155
Phosphoric acid . . . . .	1·668	0·386	traces.
Potash . . . . .	32·384	27·004	} 16·432
Soda . . . . .	17·843	8·895	
Chloride of sodium . . . . .	2·051	2·118	
<b>INSOLUBLE SALTS :</b>			
Lime . . . . .	10·204	17·366	44·936
Magnesia . . . . .	2·384	0·923	traces.
Sulphate of lime . . . . .	traces.	traces.	traces.
Phosphate of lime . . . . .	29·714	18·038	24·536
"    " magnesia . . . . .	traces.	traces.	traces.
"    " peroxide of iron . . . . .	0·332	0·645	1·077
"    " manganese . . . . .	traces.	traces.	traces.
Silicic acid . . . . .	3·420	11·931	8·539
	100·000	100·000	100·000

Upon comparing the above results, it will be seen that whilst the ashes of the leaves contained about 12½ per cent of sulphuric acid, those of the berries contained only a trace. In another analysis, however, deduced from the subsequent analyses of the sap, &c., of another sample of berries from the same tree, I found the composition of the ash to be as follows :

	As found.	After de-ducting the carbonic acid.
<b>SOLUBLE SALTS :</b>		
Carbonic acid . . . . .	12·921	—
Sulphuric acid . . . . .	10·011	12·445
Phosphoric acid . . . . .	0·846	1·041
Potash . . . . .	22·504	27·702
Soda . . . . .	12·662	15·586
Chloride of sodium . . . . .	0·486	0·598
<b>INSOLUBLE SALTS :</b>		
Carbonate of lime . . . . .	} 13·275	—
"    " magnesia . . . . .		—
Lime . . . . .	—	} 9·151
Magnesia . . . . .	—	
Sulphate of lime . . . . .	traces.	traces.
Phosphate of lime . . . . .	20·643	25·411
"    " magnesia . . . . .	traces.	traces.
"    " peroxide of iron . . . . .	2·949	3·630
"    " manganese . . . . .	traces.	traces.
Silicic acid . . . . .	3·703	4·436
	100·000	100·000

It would, perhaps, be useless in the present state of our knowledge, to attempt to give any explanation of the extraordinary discrepancy in the above results; but unless we can conceive one of the following suppositions to be correct, it would appear likely to remain perfectly unaccountable; viz: either,

1. That the organs of plants have the power of assimilating different quantities of certain inorganic substances at different periods of their development. Or,

2. That the same organs gathered from different parts of the same plant contain different inorganic constituents.

Future experiments will, however, very probably account for these, at present, inexplicable results.

Considering the proportion of sulphuric acid contained in the leaves only, it is very remarkable, that the ashes of very few plants, even among the *Cruciferae* (plants which are known to require sulphuric acid, or the sulphates for their complete development) contain more than 12·7 per cent of that acid. In order to show this more clearly, I have extracted from the works of other chemists, several instances of the maximum proportion of sulphuric acid contained in the ashes of various plants.

I.	<i>Brassica oleracea</i>	leaves	12·70	per cent.
II.	" "	"	7·06	" "
I.	<i>Brassica rapa</i>	"	14·70	" "
II.	" "	"	13·34	" "
III.	" "	"	11·12	" "
I.	" "	(root)	7·77	" "
I.	<i>Lotus uliginosus</i>	(plant)	10·16	" "
I.	<i>Medicago lupulina</i>	"	11·52	" "

It will be seen that only two of these contain more than the ashes of the mulberry leaves.

If we examine the relative proportions of the other constituents, we shall find that their distribution is in perfect accordance with the law, which I some time ago put forward in a former paper on the Inorganic Constituents of Plants, and which, after a long continued series of observations of the results obtained by myself and others, I have found to be universally followed; viz: "that the earthy salts, taken as a whole, occur in greatest proportion in the stem, less in the leaves, and least of all in the fruit, where the alkaline or earthy phosphates predominate." The subjoined table will render this more evident.

	Per centage of earthy salts.	Per centage of earthy phosphates.	Phosphoric acid in soluble salts.
Branch . .	78.007	24.536	traces.
Leaves . .	48.258	18.038	0.386
Fruit . .	45.622	29.714	1.668

As this extraordinary peculiarity, which the organs of plants possess, of selecting from among the heterogeneous mineral substances absorbed from the soil, has excited considerable attention of late, it may not be considered uninteresting to show how far this relative distribution of the phosphoric acid in the different organs extends to other vegetables. The following table exhibits the proportion of phosphoric acid in 100 of ash.

			Straw.	Seed.
* Rape . . . . .			4.76	45.95
* Peas . . . . .			9.21	40.56
† Wheat . . . . .			4.08	57.31
‡ Rye . . . . .			3.80	46.03
§ Barley . . . . .			1.80	31.20
Oats . . . . .			0.51	42.54
			Wood.	
¶ Silver Fir. <i>Pinus picea</i> . . . . .			4.49	39.65
** Scotch Fir. <i>Pinus sylvestris</i> . . . . .			1.00	45.95
			Berries.	
†† Ivy. <i>Hedera helix</i> . . . . .			9.22	26.49

Upon comparing the relative proportions of magnesia contained in the ashes of the different organs of the mulberry, we shall notice the curious fact that, like the phosphoric acid, it occurs in greatest quantity in that of the berries. This is the more remarkable inasmuch as the other earthy salts, as I before observed, are invariably present in greatest abundance in the wood. This difference in the distribution of the lime and magnesia salts does not appear to be peculiar to the mulberry, for, if we may judge from the other comparative analyses already published, it occurs to a greater or smaller extent in every plant; and although it is most particularly evident in graminaceous plants (where the proportion of magnesia in the seed is often from six to seven times as great as that in the stalk) it

\* Rammelsberg.

† Petzholdt.

‡ Fresenius and Will.

§ Way.

|| Salm-Horstmar.

¶ Levi.

\*\* Böttinger.

†† Herapath Jun.

is, without doubt, also observed in other plants; but from the paucity of our information on the subject, it would, as yet, be unwise to put it forward as a general law. It must be left for future experimenters, therefore, to demonstrate whether or not such be the case.

Notwithstanding the proportion of silica and phosphate of iron in these ashes is but small, my subsequent analyses would appear to show that they play some important part in the organism of the plant, inasmuch as I found them existing in intimate combination with the cellular tissue, or basis of the organs.

In order to discover in what state these substances—the silica particularly—occurred in the plant, I carefully incinerated a portion of a mulberry leaf on a piece of platinum foil, and after transferring the ash to a glass plate treated it with concentrated nitric acid. Upon examining the residue under a microscope of high power, I found that the silica and oxide of iron retained the exact form of the cells; proving beyond a doubt that they were either in absolute combination with the cellulose, or, that they communicated strength to the cells by being deposited on their sides.

I shall now proceed to detail the numerical results of my analyses of the ashes of the separate parts of these organs, after describing the mode of their preparation.

*Preparation of the component parts of the organs.*—A certain known quantity of each of the fresh organs was separately taken, crushed in a porcelain mortar, and the pulpy mass, thus obtained, was then subjected to pressure. The residuary mass was afterwards treated repeatedly, first with cold and afterwards with hot water. It was then digested for twenty-four hours with a weak solution of acetic acid, occasionally changing the solution, afterwards well washed with water, dried at 220° F. and weighed. This substance, which I shall call *woody matter* in the subsequent analyses, was then divided into two portions of equal weight; one of these was incinerated, and the ash weighed and analysed; the other was first digested for twenty-four hours with strong nitric acid, and, after being well washed, again digested for another twenty-four hours in a weak solution of caustic alkali, repeatedly changing the solution; it was then boiled for about a quarter of an hour in dilute hydrochloric acid. The residue, which consisted of pure cellulose, after being well washed with distilled water, was dried at 220° F. and accurately weighed. It was then incinerated, and the ash weighed and analysed. The results of this analysis, deducted from those

of the previous analysis of the woody matter gave, indirectly, the composition of the inorganic constituents of the incrusting matters.

The sap, to which the various washings, together with the acetic acid solution, had been previously added, was evaporated to dryness, and the weight of the residue accurately noted. It was then incinerated with the necessary precautions, and the weight of the inorganic residue having been determined, it was submitted to analysis.

## II.—ANALYSES OF THE ASHES OF THE COMPONENT PARTS OF THE ORGANS.

I. *Of those of the Berries.*—14449·4 grains of fresh, and partly ripe, mulberries gave 270·203 grs. of dry woody matter, which gave 10·213 grs. of ash upon incineration ; and 808·897 grs. of the dried contents of cells, which contained 92·035 grs. of inorganic substances.

These make altogether, 102·248 grs. of mineral ingredients instead of 100, as obtained by the preceding experiments.

Another 270·203 grs. of woody matter furnished 73·722 grs. of pure cellulose, which yielded 0·755 grs. of ash upon incineration. There were, therefore, 196·481 grs. of incrusting matters, containing 9·458 grs. of inorganic constituents.

I found the composition per cent of these ashes to be as follows :

	Sap as found.	Sap as calcul'd.	Sap, mean.	Woody matter.	Cellulose.	Incrusting matters.
<b>SOLUBLE SALTS :</b>						
Carbonic acid . . .	13·579	20·059	16·931	6·991	1·324	7·443
Sulphuric acid . . .	11·106	traces.	5·598	0·145	traces.	0·158
Phosphoric acid . . .	0·941	1·345	1·141	—	—	—
Potash . . . .	24·773	25·884	25·328	} 11·152	2·119	11·873
Soda . . . .	13·053	13·362	13·209		—	0·211
Chloride of Sodium .	0·518	1·632	1·070	0·180	—	—
<b>INSOLUBLE SALTS :</b>						
Carbonate of lime . .	} 12·644	16·710	14·667	18·946	6·887	19·908
" " magnesia . .		traces.	traces.	—	—	—
Sulphate of lime . .	traces.	traces.	traces.	—	—	—
Phosphate of lime . .	18·547	19·511	19·037	39·528	43·046	39·246
" " magnesia . .	traces.	traces.	traces.	—	—	—
Perphosphate of iron .	2·197	—	1·120	9·732	38·545	7·432
Silicic acid . . . .	2·642	1·497	1·899	13·326	8·079	13·729
	100·000	100·000	100·000	100·000	100·000	100·000

II. *Of those of the Leaves.*—3999·3 grains of freshly gathered mulberry leaves gave 393·7 grs. of woody matter, which yielded

24.06 grs. of ash upon incineration; and 586.1 grs. of the dried contents of cells, which gave 75.22 grs. of ash.

These make altogether, 99.28 grs. of mineral ingredients instead of 100 grs. as obtained by the preceding experiments.

Another 393.7 grs. of woody matter gave 133.561 grs. of pure cellulose, which furnished 1.457 grs. of ash when incinerated. There were therefore 260.639 grs. of incrusting matters containing 22.603 grs. of inorganic substances.

I found the composition per cent of these ashes to be as follows:

	Sap as found.	Woody matter.	Cellulose.	Incrusting matters.
<b>SOLUBLE SALTS:</b>				
Carbonic acid . . .	11.964	0.856	1.647	0.805
Sulphuric acid . . .	11.991	4.542	traces.	4.838
Phosphoric acid . . .	0.275	—	—	—
Potash . . . .	27.787	} 5.502	2.539	5.696
Soda . . . .	9.400			
Chloride of Sodium . .	2.658	—	—	—
<b>INSOLUBLE SALTS:</b>				
Carbonate of lime . .	15.981	52.722	6.794	55.707
"    " magnesia .	1.196	0.906	traces.	0.965
Sulphate of lime . .	traces.	traces.	—	traces.
Phosphate of lime . .	13.213	16.338	30.130	15.455
"    " magnesia .	traces.	—	—	—
"    " manganese .	—	traces.	—	traces.
Perphosphate of iron .	traces.	2.726	24.639	1.314
Silicic acid . . .	5.535	16.408	34.251	15.220
	100.000	100.000	100.000	100.000

*III. Of those of the Branch.*—7681.8 grains of the fresh branch gave 3158.00 grs. of dry woody matter, which yielded 60.646 grs. of ash upon incineration; and 675.3 grs. of the dried contents of the cells, which gave 44.486 grs. of ash.

These make altogether 105.132 grs. of ash instead of 100 grs. as obtained by the preceding experiments.

Another 3158. grs. of woody matter gave 779.23 grs. of pure cellulose, which furnished 3.07 grs. of ash when incinerated.

There were, therefore, 2378.77 grs. of incrusting matters, containing 56.602 grs. of inorganic substances.

I found the composition per cent of these ashes to be as follows:

	Sap as found.	Woody matter.	Cellulose.	Incrusting matters.
<b>SOLUBLE SALTS:</b>				
Carbonic acid . . .	8.583	1.975	4.104	1.893
Sulphuric acid . . .	traces.	6.170	—	6.611
Phosphoric acid . . .	traces.	—	—	—
Potash . . . .	15.664	7.932	7.426	8.097
Soda . . . .	5.007	traces.	—	traces.
Chloride of sodium . .				
<b>INSOLUBLE SALTS:</b>				
Carbonate of lime . .	51.127	55.898	38.436	53.953
, , magnesia . .	traces.	—	—	—
Sulphate of lime . .	traces.	—	—	—
Phosphate of lime . .	19.619	11.944	—	17.730
, , magnesia . .	traces.	—	—	—
, , manganese . .	—	traces.	—	traces.
Perphosphate of iron . .	4.597	—	—	0.037
Peroxide of iron . . .	—	—	38.436	—
Silicic acid . . . .	11.484	11.598	—	11.679
	100.000	100.000	100.000	100.000

The calculated composition of the inorganic constituents of the sap of the present and preceding organs, differed so slightly from that actually found, that I have considered it quite unnecessary to give the calculations.

From the data contained in the preceding pages, the three following tables have been calculated:

TABLE I.

SHOWING THE RATIO OF THE CELLULOSE TO THE OTHER ORGANIC PARTS IN THE DIFFERENT ORGANS.

	Proportion in grains of dried organic parts in 1000 <sup>0</sup> grs. of fresh organs.			Proportion in grains of dried organic parts in 1000 <sup>0</sup> grs. of dried organs.			Ratio of the cellulose to the other organic parts.		
	Berries.	Leaves.	Branch.	Berries.	Leaves.	Branch.	Berries.	Leaves.	Branch.
Cellulose . . . .	5.10	33.3	101.43	68.4	136.1	203.2	1.00	1.00	1.00
Incrusting matters . .	13.60	65.1	309.68	182.0	265.8	620.8	2.66	1.94	3.05
Sap or contents of cells . .	55.98	146.5	87.99	749.6	598.1	176.0	10.97	4.38	0.86
Woody matter . . . .	18.70	98.4	411.11	250.4	401.9	824.0	—	—	—

TABLE II.

SHOWING THE PROPORTION OF ASH OBTAINED FROM THE DRIED ORGANS  
AND ORGANIC PARTS.

	Weight in grains of ash obtained from 1000· grs. of dry organs, &c.	Weight in grains of dried organs, &c. requisite to produce 100· grs. of ash.
Entire organ :		
Berries . . . . .	92·660	1079·1
Leaves . . . . .	102·050	979·8
Branch . . . . .	26·087	3833·3
ap, or contents of cells of :		
Berries . . . . .	112·800	886·5
Leaves . . . . .	128·300	779·1
Branch . . . . .	58·270	1716·0
Cellulose from :		
Berries . . . . .	10·240	9764·5
Leaves . . . . .	10·900	9167·9
Branch . . . . .	3·951	25307·4
Incrusting matters from :		
Berries . . . . .	48·180	2077·4
Leaves . . . . .	77·870	1284·1
Branch . . . . .	24·260	4131·2
Woody matter from :		
Berries . . . . .	37·790	2646·2
Leaves . . . . .	61·110	1628·0
Branch . . . . .	19·210	5207·0

TABLE III.  
SHOWING THE COMPOSITION PER CENT OF THE ASHES OF THE COMPONENT PARTS OF THE ORGANS, AFTER DEDUCTING THE CARBONIC ACID.

	Sap of berries, mean.	Sap of leaves.	Sap of branch.	Woody matter of berries.	Woody matter of leaves.	Woody matter of branch.	Cellulose of berries.	Cellulose of leaves.	Cellulose of branch.	Incrust-ing mat-ers of berries.	Incrust-ing mat-ers of leaves.	Incrust-ing mat-ers of branch.
<b>SOLUBLE SALTS:</b>												
Sulphuric acid	7.121	14.918	traces	0.171	6.018	8.402	traces	—	—	0.188	6.520	8.893
Phosphoric acid	1.451	0.342	traces	—	—	—	—	—	—	—	—	—
Potash	32.232	31.569	22.727	{ 2.416 10.754 }	7.290	10.801	2.215	2.662	9.401	14.134	7.678	10.865
Soda	18.907	11.694	traces	0.212	—	—	—	—	—	0.251	—	traces
Chloride of Sodium	1.361	3.306	7.264	—	—	—	—	—	—	—	—	—
<b>INSOLUBLE SALTS:</b>												
Lime	10.447	{ 11.134 0.709 16.438 }	41.542	12.530	39.119	42.629	4.032	3.989	27.252	13.510	42.055	40.619
Magnesia	24.716	28.467	traces	—	0.572	traces	—	traces	—	—	0.620	—
Phosphate of lime	traces	traces	traces	—	21.515	16.279	44.205	31.594	—	—	46.722	20.836
" " magnesia	traces	traces	traces	—	—	—	—	—	—	—	—	23.844
" " manganese	traces	traces	traces	—	11.493	3.611	6.260	40.299	25.836	—	8.847	17.71
" " peroxide of iron	1.424	—	traces	—	—	—	—	—	—	—	—	—
Peroxide of iron	—	traces	traces	—	—	—	—	—	—	—	—	—
Sulphate of lime	6.890	—	traces	—	15.742	21.875	15.629	9.249	35.919	14.683	16.348	20.520
Silicic acid	2.341	—	—	—	—	—	—	—	—	—	—	15.729
	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000

Upon comparing the results contained in the second table, the vast difference in the proportion of the ash yielded by the different organs is immediately perceptible; thus, whilst the branch contained 2·6 per cent of inorganic constituents, the leaves and berries contained respectively 10·2 and 9·2 per cent. These differences are evidently, in a great measure, occasioned by the great amount of evaporation that occurs from the two last mentioned organs as compared with the former, which tends to concentrate the non-volatile constituents of the sap, and, thereby, the inorganic substances. This, as might be anticipated, does not occur in the present instance only; it has been found to be a general law throughout the whole vegetable kingdom. I have extracted a few of the most striking results from the works of various chemists which will exemplify this:

	Ash per cent.
* Oak leaves, ( <i>Quercus robur</i> ) . . . . .	5·300
,, branch     ,,     ,, . . . . .	0·400
* Poplar leaves, ( <i>Populus alba</i> ) . . . . .	9·300
,, branch     ,,     ,, . . . . .	0·800
* Hazel leaves, ( <i>Corylus avellana</i> ) . . . . .	6·100
,, branch     ,,     ,, . . . . .	0·500
* Beech leaves, ( <i>Fagus sylvatica</i> ) . . . . .	6·695
,, branch     ,,     ,, . . . . .	0·365
† Parsnip leaves, ( <i>Pastinaca sativa</i> ) . . . . .	15·761
,, root       ,,     ,, . . . . .	4·643
† Carrot leaves, ( <i>Daucus carota</i> ) . . . . .	10·425
,, root       ,,     ,, . . . . .	5·090

Again, it will be seen on reference to the same table, that in all the organs, the sap furnished a much greater proportion of ash than the respective woody matter; and, we shall also see upon reference to the third table, that whilst the ashes of the former were more than half composed of alkaline salts, those of the latter contained, comparatively, only a very small quantity, consisting almost entirely of insoluble earthy and metallic salts; thus, the alkaline salts of the ashes of the sap were to those of the ashes of the woody matter, of the different organs examined, as follows: in the berries as 61· grs. to 13·5 grs.; in the leaves as 65· grs. to 13·5 grs.; and in the branch as 30· grs. to 19·25 grs.

Now as it has been long since proved by other experimenters, that the deposition of the incrusting matters increases with the age of

\* Those analyses marked with an \* are by Théodore de Saussure, and those with a † by Sprengel.

plants, we should expect to find, judging from the preceding analyses, that although the total amount of the solid matters of a plant would be greater at the later periods of its growth, the relative proportion of the inorganic constituents would be actually diminished; and, also, that there would, at the same time, be a more considerable deposition of insoluble earthy and metallic salts in the tissues; and such is found to be the case, as the subjoined table will show:

	Ash per cent.	Weight in grs. of insoluble salts in dried plant. 100 grs. of ash.
<i>Solidago virgaurea</i> , before flowering . . . . .	9·2	32·50
" " when in flower . . . . .	5·7	41·00
" " after flowering . . . . .	5·0	52·00
<i>Helianthus annuus</i> , before flowering . . . . .	14·7	37·00
" " when in flower . . . . .	13·7	39·00
" " after flowering . . . . .	9·3	48·50
<i>Pisum sativum</i> , when in flower . . . . .	9·5	50·20
" " after flowering . . . . .	8·1	65·75
<i>Vicia faba</i> , before flowering . . . . .	15·0	44·50
" " when in flower . . . . .	12·2	44·50
" " after flowering . . . . .	6·6	50·00
<i>Triticum hyburnum</i> , before flowering . . . . .	7·9	40·00
" " when in flower . . . . .	5·4	59·00
" " after flowering . . . . .	3·3	90·00

If this reasoning be correct, we should likewise expect to find the same occur in the development of the wood itself; and here also we find it fully borne out as the following results of Saussure and myself will prove.

	Saussure.		Herapath, Jun.	
	Ash per cent.	Insoluble salts.	Ash per cent.	Insoluble salts.
<i>Mulberry albumnum</i> , or sap-wood . . . . .	1·3	74·0	3·60	56·
" <i>duramen</i> , or heart-wood . . . . .	0·7	79·0	0·80	81·3

Many other analyses of the ashes of different kinds of wood might be brought forward in support of this theory, did I not consider them quite unnecessary.

A glance at the results of the analyses, given in the third table, will alone suffice to render the great difference in the composition of the inorganic constituents of the cellulose of the different organs examined, immediately evident. These differences are, without doubt,

in a great measure occasioned by the cellulose of the branch having been subjected to a more perfect purification than that from the berries or leaves. For I found that the cellulose prepared from the last mentioned organs with nitric acid alone, contained a much larger proportion of inorganic constituents than that obtained from the same organs by the process before described; and these ashes likewise differed very materially in composition, as will be seen on comparing the subjoined analyses with those previously given (Table III.)

	Berries.	Leaves.
Sulphuric acid . . . . .	traces	traces
Potash }	4.090	3.736
Soda }		
Lime . . . . .	54.858	27.903
Phosphate of iron . . . . .	36.488	15.376
Perphosphate of lime }		23.084
Silicic acid . . . . .	4.564	29.901
	100.000	100.000

These and the preceding analyses, imperfect though they are, clearly demonstrate that inorganic substances do sometimes exist in actual combination with the elementary tissues of plants. It still remains, however, for future experimenters to prove whether such is always the case, and if so, whether any fixed and general laws are observed in their distribution.

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Feb. 21, 1848.

The President in the chair.

J. Philips, Esq. was elected a member of the Society.

The Council, in accordance with the laws, proposed the following gentlemen as Vice-President and Members of Council for the ensuing year, in place of those retiring : Henry Beaumont Leeson, M.D. as Vice-President, and Thos. Andrews, M.D., Benjamin Brodie, Esq., J. J. Griffin, Esq., Edward Solly, Esq. as Members of Council. Edmund Ronalds, Ph. D. was also nominated to succeed George Fownes, Ph. D. who resigns from bad health.

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March 6, 1848.

E. F. Teschemacher, in the Chair.

Dr. Hare, of Pennsylvania, presented numerous copies of his Essay,

entitled "Objections to the Theories of Franklin, Dufay and Ampère, with an effort to explain Electrical Phenomena by Statical or Undulatory Polarization," to the Society's library, and for distribution to the members.

Dr. Playfair exhibited the aneroid barometer, with a table of results from comparative observations made with a standard barometer to demonstrate its accuracy.

The following communication was read :

*XI.—On the preparation of the Prussian Blue, generally known as "Turnbull's Blue."* By ROBERT WARINGTON, Esq.

In bringing the present notice before the Society, I feel it necessary to apologise for introducing a subject to their attention which has been so ably investigated by many of our most eminent chemists, and the results of whose labours are to be found in the Chemical Manuals of the present day. Yet, when we find substances in commerce, under this title, or under the various magnified appellations of "Egyptian blue," "Cerulean blue," &c., differing exceedingly in character from each other, some of them of great beauty in colour, and frequently possessing modified properties; when the difficulty attending the preparation of this blue of an uniform tint, which is a great source of annoyance to many of the makers, is also taken into consideration, I am induced to believe that the results of the investigation may not be deemed uninteresting to the Members of this Society, or unimportant to the manufacturing chemist. The greater part of the experiments were made in the year 1834, and many of them have been lately repeated, the investigation has also been extended, for the purpose of confirmation, before being submitted to the Society.

I must premise, that the great object in view in commencing this investigation, was the production of a colour analogous to what was then known as "Turnbull's blue," and was, at the period I allude to, made, I believe, only by the firm of Turnbull and Ramsay, of Glasgow; its extreme beauty, and the bright, metallic, coppery lustre exhibited on its surface, will be well known to most of our Members. I need hardly say that numerous unsuccessful experiments were made before anything approaching the desired tint was obtained. Its attempted production from a persalt of iron by various and modified processes was unsuccessful in every case; nothing comparable with it in lustre or beauty was obtained. After trying the different persalts of iron, the method of peroxidizing the protosalt was varied, and this was followed by the action of the ferridcyanide of potassium on the protosalt, in place of the ferrocyanide on the persalt, but the result was still not perfectly satisfactory.

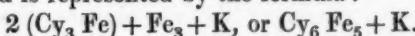
In the course of these experiments, however, certain points were noted, which ultimately led the way to the desired result ; one of the principal of these, and that which bears most fully on the present subject, was the fact, that the precipitate produced by a solution of the ferrocyanide of potassium in the solution of a protosalt of iron, has a most powerful affinity for oxygen ; every one must be aware of this to a certain extent, inasmuch as the precipitate absorbs oxygen from the air, and becomes deepened in colour ; but so energetic is this attraction, that many solutions of the salts of metallic oxides are deoxidized rapidly and perfectly when brought within the sphere of its action ; many of the blue salts of copper are rendered colourless, salts of chromic acid are reduced to salts of the green oxide, sufficient acid being present to hold in solution the protoxide of chromium which is produced ; salts of peroxide of tin, mercury, and iron are also rapidly reduced to the state of protosalts.\*

The precipitate, in either of these cases, darkens and becomes gradually of a deep blue colour, which is more or less intense as the quantity of the metallic salt, or the proportion of oxygen contained in it, varies ; the fine, metallic, coppery lustre is at length gradually developed. As this effect could thus be produced by salts of a metallic oxide, there was no apparent reason why the same result should not be arrived at with solutions of other agents containing oxygen either in large quantity or feebly combined, as for instance, in chloric acid and its salts, and in chlorous acid.

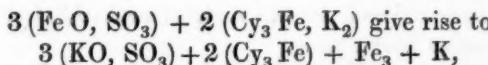
Another point was also rendered evident from the above experiments, namely, that it was actually necessary that the precipitate formed in the protosalt of iron by ferrocyanide of potassium should first be produced in order to obtain the state of molecular aggregation in the compound capable of yielding a blue of the fine colour and lustre sought, and upon which, as a basis, the effect of oxidizing agents could be fully developed. The composition of this precipitate,

\* I may mention here that this re-action with the salts of iron affords an excellent means of securing a solution of this metal in the state of protoxide for the purpose of exhibiting its peculiar reactions in the Class-room, experiments which are at times attended with some little annoyance. For this purpose a solution of the ordinary protosulphate of iron is to be partially precipitated, in a well-corked or stoppered bottle, by a solution of the ferrocyanide of potassium, and the precipitate allowed to subside ; it will then be found that this precipitate has reduced the remaining part of the solution to the state of protosulphate most perfectly, and that this is now capable of yielding a pure white precipitate, both with solutions of the carbonated alkalies and with additional solution of the ferrocyanide of potassium. The same effect may be produced by adding a portion of the recently precipitated ferrocyanide of iron to a solution of sulphate of iron.

or white Prussian blue, has been pretty well ascertained by numerous investigators and is represented by the formula :



It is produced by the action of two equivalents of the ferrocyanide of potassium upon three equivalents of the protosulphate of iron ; thus :



or sulphate of potash and the white Prussian blue.

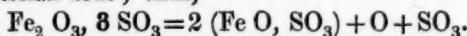
Now the question arises, as to what chemical action takes place during the darkening in colour or oxidation of this compound through the medium of oxidizing agents, and I shall presently be able to show, that it is the conversion of the equivalent of potassium, which forms one of its ingredients, into potash, and the removal of the potash at the same time, by the agency of an acid, with which it is able to combine. I have already shewn that there are various agents by which this oxidation may be effected ; those which I have found to answer the purpose most efficiently, are : 1st. the bichromate of potash ; 2nd. the chlorate of potash ; 3rd. a soluble persalt of iron ; 4th. chlorinated soda, or a solution of chloride of lime.

When bichromate of potash is employed, it is necessary to use one-third of an equivalent only, as the salt will afford three equivalents of available oxygen, and to effect our object perfectly, one only is required ; thus,

$\text{KO, } 2\text{CrO}_3 + 4\text{SO}_3$  will yield  $(\text{KO, SO}_3 + \text{Cr}_2\text{O}_3, 3\text{SO}_3) + \text{O}_3$  or one equivalent of bichromate of potash treated with four equivs. of sulphuric acid, will give rise to one equiv. of sulphate of chromium and potash (chrome alum) and three equivs. of oxygen, and as the single equivalent of potassium we wish to oxidize requires only one equiv. of oxygen, the third part of an equiv. of the bichromate will suffice for our purpose ; an additional equivalent of sulphuric acid is, however, indispensable for the purpose of uniting with the potash resulting from this oxidation.

When chlorate of potash is used as the oxidizing agent, about one-fifth of an equivalent is sufficient for the oxidation, the requisite proportion of hydrochloric acid being added to decompose the salt, and set the chloric acid free ; as in the former case, care must be taken that an equivalent of sulphuric acid is present, to combine with the resulting potash. The same remarks will equally apply to the employment of chlorinated soda or chloride of lime ; the latter compound, however, is objectionable from the sulphate of lime which is necessarily produced when protosulphate of iron or

sulphuric acid is made use of in the operation. In the third case, where a persalt of iron is the oxidizing medium, and in these experiments I have always employed the persulphate, the preparation of which will be immediately described, a single equivalent is necessary to yield the one equiv. of oxygen, and sufficient sulphuric acid is contained in this solution to combine with the oxidized potassium after the iron has been reduced to the state of protoxide by the action of the white Prussian blue; thus,



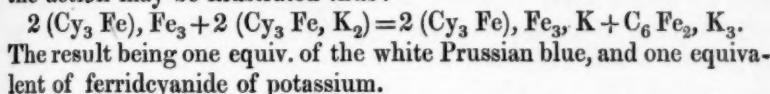
That this action is owing to the oxidation and subsequent removal of the equivalent of potassium, will, I think, be evident from the fact, that when the bichromate of potash is employed in the proportion stated, the supernatent liquor has the pinkish-blue colour of the double sulphate of chromium and potash; but if more than this be used, a portion of bichromate remains in solution, exhibiting its characteristic orange-colour. The same remarks apply to the persalt of iron, any excess above the equivalent required, being found in the filtrate or supernatent liquor when the Prussian blue has subsided.

To prepare the persulphate of iron, I have found that either bichromate of potash or chlorate of potash may be employed with much greater advantage than nitric acid; care must be taken that sufficient sulphuric acid is present to hold the peroxide of iron produced in solution; and also, in the first case, to form chrome alum with the deoxidized chromic acid; the decomposition of the chlorate of potash should always be effected by hydrochloric acid. Now as the protosulphate of iron assumes an additional half equivalent of oxygen to form persulphate, it will be evident that one-sixth of an equivalent of bichromate of potash, or one-tenth of an equivalent of chlorate of potash with the requisite proportion of acid will be sufficient for this conversion. When the oxidizing solution is prepared with chlorate of potash, the solution, after the oxidation of the white Prussian blue, may be precipitated by ferrocyanide of potassium for a future operation; if bichromate has been used, the protoxide of chromium will, to a certain extent, be precipitated by the ferrocyanide of potassium, and interfere with the brilliancy of the subsequent colour.

The white Prussian blue should be precipitated from dilute solutions in order to obtain an uniform product in the proper state of aggregation. I find that when the materials are respectively dissolved in about ten times their weight of water, a very good result is obtained.

It is well known that when Turnbull's blue is digested in a

solution of the ferrocyanide of potassium, a pale or white Prussian blue and ferridcyanide of potassium result; this is best effected by acting on one equivalent of the former with two of the latter, and the action may be illustrated thus:



March 21, 1848.

The President in the Chair.

Dr. Edward Schunk presented his Essay "On Madder" to the Library.

Messrs. F. A. Abel, Thomas H. Rowney, and Robert Richardson were duly elected Members of the Society, and Messrs. Robert Murray and J. G. Latta as Associates.

The following papers were read:

XII.—*Researches on Atomic Volume and Specific Gravity, by JAMES P. JOULE, Esq. Corresponding Member of the Royal Academy of Sciences, Turin, and LYON PLAYFAIR, F.R.S. of the Museum of Practical Geology.*

#### SERIES IV.—EXPANSION BY HEAT OF SALTS IN THE SOLID STATE.

In pursuing our researches on atomic volume and specific gravity, we have thought it desirable, as has been already intimated in a previous memoir, to ascertain the expansion of the salts by heat, as well as their volume at a given temperature. In this way we hope to arrive ultimately at the solution of the apparent discrepancies between theory and experiment. We are not aware that any experiments of this kind have hitherto been made. Brunner has indeed determined the expansion of ice, and we are led to expect that Pierre, who has already given valuable results on the expansion of liquids, will extend his labours to solid salts. We hope, therefore, that our own results, as detailed in the present memoir, will be speedily confirmed. The expansion of solids by heat is a subject which although little cultivated hitherto, is of very great importance to science, and will require, in all probability, the labours of many experimenters for its complete development. It will not, therefore, be expected that we shall be able to include the expansions of the whole range of known inorganic salts in one memoir; our object being simply to examine a sufficient number of them, in order to throw light on the causes

which produce variations in the sp. gr. of bodies, and thus enable us to confirm or correct our views on atomic volumes.

It was only after much consideration and some preliminary trials, that we were enabled to select what appeared to us an unexceptionable method of conducting the experiments. The first form of apparatus which suggested itself to us, consisted of a glass volumenometer, Fig. 1, in which *a* is a bulb, of two and a half cubic inches capacity, having a neck fitted with a perforated glass stopper *b*. A graduated tube *c d*, of small diameter, was attached to this bulb,

FIG. 1.

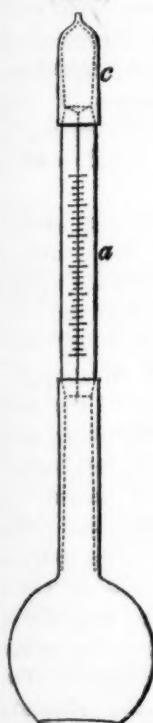


having at the centre a smaller bulb, of one cubic inch capacity. A syringe was attached tightly to the extremity, and the whole was immersed in a large vessel containing water. The method of experimenting with this apparatus was as follows:—The bulb *a* was filled with turpentine or any liquid incapable of dissolving the salt, and the exact quantity was noted on the graduated stem at *c*. The piston of the syringe was then gradually withdrawn, so as to draw the liquid nearly to the end of the tube *d*, entirely filling the intermediate bulb. A known quantity of the salt was then thrown into the bulb *a*, and the stopper being re-adjusted, the liquid was driven back by the syringe till it ascended into the perforation of the stopper. By examining the position of the liquid in the graduated tube, the space occupied by the salt was rendered evident. By conducting experiments with a salt in the above manner, at different temperatures, its expansion could be made evident, regard being of course paid to the expansion of the glass tube.

Several trials were made with the above-described apparatus, the use of which appeared to offer a great advantage in not requiring an acquaintance with the expansion of the liquid employed. However, it was speedily found that there were grave inconveniences attending it, in consequence of the difficulty of drying the tube thoroughly after each experiment, as well as the danger of losing a portion of the salt whilst introducing it through the narrow neck of the bulb. But these objections might have given way to time and patience. Our chief, and with this apparatus, insurmountable difficulty, arose from the fact, that a quantity of air always remained attached to the

salt after immersion. Since, therefore, it was highly probable that the quantity of adhering air varied with the temperature, the apparatus appeared liable to error, and was consequently abandoned.

FIG. 2.



After some other attempts, we at last fixed upon a plan, which appeared to combine the advantages of accuracy with great practical facility. We procured four sp. gravity bottles, made of the same sample of glass. Two of them, marked No. 1 and No. 3, were capable of containing somewhat more than 500 grs. of water, whilst the other two, No. 2 and No. 4, had a capacity for about 270 grs. of water, the latter being destined for ascertaining the volumes and expansions of weighty articles in small quantities. We have given a half-size representation of one of the larger bulbs in Fig. 2, where *a* is a stopper formed from a piece of thermometer tube of narrow bore, terminated at the upper end by a small conical cavity, over which a cap *c* is accurately fitted by grinding, so that any liquid which may have ascended through the capillary, is confined in the cap without loss. There is a fine capillary perforation at the summit of the cap, for allowing the egress of the air displaced by the liquid.

In order to ascertain the expansion of the glass of these volumenometers, the capillary tubes which served for their stoppers were carefully calibrated and graduated. They were then filled with distilled water and immersed for half an hour in a bath containing a large quantity of water, kept constantly at  $38^{\circ}92$  (F). The exact height of the water in the capillary tube being then noted, the water in the bath was from time to time increased in temperature. At every successive increase, the position of the water in the stem was observed. It first descended and then of course ascended, until at the temperature of  $45^{\circ}82$ , the water stood at exactly the same point as at  $38^{\circ}92$ . Hence it was evident that the glass had expanded exactly as much as the water, through the interval between  $38^{\circ}92$  and  $45^{\circ}82$ . According to the table given by Despretz, it appears that the expansion of water through this interval is  $0\cdot0001069$ ; so that, supposing the expansion of glass to go on at the same rate through  $180^{\circ}$ , the expansion of the bulbs of the volumenometers will be  $0\cdot002788$  between the freezing and boiling points of water.

Another experiment of the same kind showed that the expansions of the glass and water were the same through the interval between  $38^{\circ}478$  and  $46^{\circ}218$ , which placed the expansion of the volumenometers at 0.002798.

The expansion of the glass bulbs being thus known, it was easy to see how they might be employed in ascertaining the expansion of turpentine and salts. For by weighing them filled with turpentine, at different temperatures, we could obtain the expansion of that fluid. And then by weighing the bulbs filled with turpentine, and a given weight of salt at different temperatures, we could readily obtain the volume and expansion of the salt.

It need hardly be observed, that experiments of this nature require to be performed with very great accuracy. We therefore employed an excellent calibrated thermometer, in which each division was equal to  $\frac{1}{12.92}$  of a degree, of Fahrenheit's scale, and the freezing point, which had remained nearly stationary, for half a year stood at 16.1 divisions. It was easy to read off temperatures to within  $\frac{1}{150}$ th of a degree by this instrument. We also employed a very sensible balance by Dancer, which would turn well with the addition of  $\frac{1}{1000}$ th of a grain, when each scale was loaded with 1000 grs. The barometric pressure was always noted, in order to correct the observed weights, and before weighing, the bulbs were reduced nearly to the temperature of the apartment, to prevent the inaccuracy arising from the currents of air they would otherwise occasion in the balance case. In taking temperatures, regard was had to the temperature of that part of the stem not immersed in the bath; and, whenever necessary, the rule of the committee of the Royal Society was employed in order to supply the requisite correction.

In the first place the weights of the bulbs, both empty and filled with water, were ascertained, in order to find their exact capacity. The water employed for this purpose was distilled, and had been recently boiled. The stoppers were placed in the necks of the bulbs, causing the water to ascend through the capillary tubes into the small cavities at the tops of the stoppers. A noose of string was now placed on the neck of each of the bulbs, which were then immersed to within an inch of the tops of the stoppers in the bath of water. The thermometer in the bath stood at the 113th division, and kept as nearly as possible at that point for about three quarters of an hour, during the whole of which time the water was repeatedly agitated by a stirrer. Experience had already shown that three quarters of an hour was more than sufficient to reduce the temperature of the bulbs to the exact tempera-

ture of the bath ; the water remaining in the cavities at the tops of the stoppers was therefore now removed by means of bibulous paper, and the caps were placed upon them. The bulbs were then removed in succession from the bath, reduced to the temperature of the room, dried with a soft silk handkerchief, and weighed. The results corrected for barometrical pressure were as follows :

	No. 1. Volumenometer.	No. 2. Volumenometer.	No. 3. Volumenometer.
Bulbs and water at 113 . . .	623.572	882.042	922.522
Bulbs alone . . . . .	349.546	377.036	397.649
Capacity in grs. of water at 113	274.026	505.006	524.873

The bulbs being now thoroughly dried, were filled with the turpentine destined for the experiments. The range of temperature fixed upon was between about 100 and 750 of the thermometer, corresponding to about 38°.5 and 88°.8 Fahr. The low temperature was attained by dissolving carbonate of soda in the water of the bath, adding a small quantity from time to time, to keep the temperature uniform. The high temperature was maintained by a lamp, burning underneath the bath. When, after half an hour's immersion, the turpentine had attained the exact temperature of the bath, the bulbs were successively weighed, as in the case of the trial with water already described. The bulbs were then again immersed in the bath for half an hour, and re-weighed, in order to preclude the possibility of an accidental error.

Volumeno- meter.	Temp.	Weight.	Mean temp.	Mean weight.	Weight of empty bulbs.	Weight of turpentine only
No. 1	120	589.648	123.5	589.616	349.546	240.070
	127	589.584				
	745.2	583.854				
No. 2	750.4	583.802	747.8	583.828	349.546	234.282
	107.6	819.779	111.8	819.710	377.036	442.674
	116.0	819.640				
No. 3	744.5	808.874	747.45	808.831	377.036	431.795
	750.4	808.788				
	106	857.852	110.5	857.773	397.649	460.124
	115	857.694				
	744.9	846.456	747.55	846.411	397.649	448.762
	750.2	846.366				

The above results were obtained on the 11th of August, 1846, and immediately afterwards the experiments on the expansion of salts were commenced, and continued until the 26th of August, when the

turpentine (which was kept in a large glass bottle, holding about a gallon) was again tested, in order to ascertain whether any change had taken place in its density. Such was found to have happened, in consequence of the absorption of atmospheric air, as will be seen by the results given below.

Volumeno-meter.	Temp.	Weight.	Mean temp.	Mean weight.	Weight of empty bulb.	Weight of turpentine alone.
No. 1	93	590.052	93.5	590.052	349.546	240.506
	94	590.052		590.052	349.546	237.674
	399.9	587.214	399.7	587.220	349.546	234.380
	399.5	587.227				
No. 2	754.4	583.906	752.5	583.926	349.546	234.219
	750.6	583.946		583.926	349.546	238.014
	93.9	820.271	95.1	820.255	377.036	431.926
	96.4	820.239		820.255	377.036	438.219
No. 3	399.6	815.044	399.3	815.050	377.036	455.258
	399	815.056		815.050	377.036	460.704
	752.8	808.934	751.3	808.962	377.036	448.933
	749.9	808.991		808.962	377.036	448.219
No. 4	93.8	858.358	94.2	858.353	397.649	486.554
	94.7	858.349		858.353	397.649	483.909
	399.9	852.905	399.7	852.907	397.649	486.554
	399.5	852.909		852.907	397.649	483.909
No. 5	753.5	846.554	751.8	846.582	397.649	486.554
	750.2	846.610		846.582	397.649	483.909

In the above table we have recorded observations taken at a temperature intermediate between the two extremes. The same was done in the case of a large proportion of the salts tried, with a view to ascertain whether their expansion was uniform. Such appeared to be invariably the case; at least if any discrepancy occurred, it was within the limits of experimental errors. We have not, however, thought it right to extend our paper, already too voluminous, by these details. It will be seen from the observations on the volume of turpentine at the three temperatures above given, that that fluid is remarkably uniform in its expansion, a circumstance which eminently adapts it for experiments on the expansion of salts.

Owing to the slight change which had occurred in the density of the turpentine, we calculated the expansion of the salts first tried by the first table of results on the expansion of turpentine, and that of the salts last tried by the last table, employing the mean of the two tables for the intermediate experiments.

In trying a salt, the bulb, partially filled with turpentine, was accurately weighed. A quantity of salt having been then introduced,

the bulb was again weighed, the increase of weight giving the exact quantity of salt, attention being paid to the correction for barometrical pressure. The bulb was then placed under the exhausted receiver of an air-pump, until the air adhering to the salt was entirely boiled away. This done, the vacant space in the bulb was filled up with turpentine, and the stopper inserted. The weights of the volumenometers and their contents at different temperatures were then ascertained, as in the case of the experiments with turpentine alone, already described. We may mention in this place that, for convenience sake, two or three bulbs containing different salts were always tried at the same time.

Exp<sup>t</sup>. 1.—634·200 grs. of Powdered Red Oxide of Mercury, in No. 3 Volumenometer.

Temp.	Weight.	Mean Temp.	Mean Weight.
108	1442·086	109	1442·072
110	1442·058		
747·9	1431·882	748·5	1431·863
749·2	1431·844		

In calculating the volume and expansion of the red oxide of mercury from the above results, we proceeded as follows. From our first table of results for the expansion of turpentine, it appears that the weights of No. 3 volumenometer, filled with turpentine at the temperatures 110·5 and 747·55, are respectively 857·773 and 846·411. Hence, at the temperatures of the above experiment (109 and 748·5), the weights would have been 857·800 and 846·394. Subtracting the weight of oxide from the weights of the volumenometer at the two temperatures, we have  $1442\cdot072 - 634\cdot200 = 807\cdot872$  and  $1431\cdot863 - 634\cdot200 = 797\cdot663$ . These numbers being subtracted from 857·800 and 846·394, leave 49·928 and 48·731 as the quantities of turpentine displaced by the oxide at the respective temperatures. But from the first table of the expansion of turpentine, it appears that 48·731 grs. at 748·5 are equivalent to 50·008 grs. at 109, regard being had to the expansion of glass. The expansion of the oxide for the interval of temperature between 109 and 748·5 is therefore 0·001596, which gives 0·005802 as the expansion for an interval of 2325 divisions of the thermometer corresponding to 180° Fahrenheit.

It appears also that the volume of 634·200 grs. of the oxide is equal to the volume of 49·928 grs. of turpentine at 109. But from the relative weights of the volumenometer containing water and turpentine, already given, we find that the sp. gravity of turpentine at 109 is to that of water at 107·7 as 0·87669 is to 1. Hence we

readily find that the sp. gravity of the oxide at 107·7, the point of maximum density of water, is 11·136.

Expt. II.—540·940 grs. of Sulphuret of Lead in powder in No. 2 Volumenometer :

Temperature.	Weight.	Mean Temp.	Mean Weight.
108·2	1292·228}	111·3	1292·172
114·4	1292·116}		
748·2	1282·824}	748·9	1282·807
749·6	1282·791}		

Therefore expansion for  $180^{\circ} = 0\cdot01045$ . Sp. gr. at  $39^{\circ}\cdot 1 = 6\cdot9238$ .

Expt. III.—585·500 grs. of Bichromate of Potash in small crystals in No. 3 Volumenometer :

111·2	1252·440}	112·7	1252·421
114·2	1252·402}		
749·8	1245·290}	749·3	1245·297
748·9	1245·303}		

Therefore expansion for  $180^{\circ} = 0\cdot0122$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot692$ .

Expt. IV.—146·355 grs. of pounded Muriate of Ammonia in No. 2 Volumenometer :

111·8	882·348}	113·8	882·329
115·8	882·310}		
750	873·149}	749·5	873·149
748·8	873·150}		

Therefore expansion for  $180^{\circ} = 0\cdot0191$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot5333$ .

Expt. V.—376·520 grs. of Peroxide of Tin in powder. No. 1 Volumenometer :

109·2	917·088}	111·1	917·073
113	917·058}		
750	912·379}	749·5	912·381
749	912·383}		

Therefore expansion for  $180^{\circ} = 0\cdot00172$ . Sp. gr. at  $39^{\circ}\cdot 1 = 6\cdot7122$ .

Expt. VI.—405·131 grs. of Sulphate of Iron, prepared by pounding, and pressing between bibulous paper, in No. 3 Volumenometer :

104	1074·826}	107·5	1074·792
111	1074·758}		
749·4	1077·586}	750	1077·576
750·6	1077·567}		

Therefore expansion for  $180^{\circ} = 0\cdot01153$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot8889$ .

Expt. VII.—426·672 grs. of Sulphate of Copper, prepared by pressing the pounded salt between folds of bibulous paper. No. 2 Volumenometer :

Temperature.	Weight.	Mean Temp.	Mean Weight.
104·5	1083·046	108·2	1083·004
112	1082·963		
749·6	1075·777	750	1075·776
750·4	1075·775		

Therefore expansion for  $180^{\circ} = 0\cdot009525$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot 2901$ .

Exp<sup>t</sup>. VIII.—552·605 grs. of Protoxide of Lead in powder in No. 1 Volumenometer :

103·5	1090·670	106·4	1090·649
109·4	1090·629		
749·6	1085·902	750	1085·900
750·4	1085·898		

Therefore expansion for  $180^{\circ} = 0\cdot00795$ . Sp. gr. at  $39^{\circ}\cdot 1 = 9\cdot 3634$ .

Exp<sup>t</sup>. IX.—327·760 grs. of Sulphate of Magnesia, prepared by pressing the pounded salt between folds of bibulous paper. No. 3 Volumenometer :

90	1014·948	93·3	1014·913
96·6	1014·879		
750	1007·181	749·5	1007·182
749	1007·182		

Therefore expansion for  $180^{\circ} = 0\cdot01019$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot 6829$ .

Exp<sup>t</sup>. X.—417·706 grs. of Nitrate of Potash in No. 2 Volumenometer :

89·4	1063·822	93·4	1063·776
97·4	1063·731		
750·3	1056·109	749·4	1056·114
748·6	1056·119		

Therefore expansion for  $180^{\circ} = 0\cdot01967$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot 1078$ .

Exp<sup>t</sup>. XI.—287·080 grs. of Copper, prepared from the oxide by passing hydrogen over it at a red heat, in No. 1 Volumenometer :

89	846·962	92·3	846·932
95·6	846·903		
401·2	844·420	400·6	844·426
400	844·432		

Therefore expansion for  $180^{\circ} = 0\cdot0055$ . Sp. gr. at  $39^{\circ}\cdot 1 = 8\cdot 367$ .

Exp<sup>t</sup>. XII.—621·528 grs. of Yellow Chromate of Potash in No. 3 Volumenometer :

91·4	1278·445	95·2	1278·402
99	1278·360		
752·5	1271·323	752·8	1271·304
753·2	1271·285		

Therefore expansion for  $180^{\circ} = 0\cdot01134$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot 7110$ .

Expt. XIII.—531·794 grs. of Nitrate of Soda in No. 2 Volumenometer :

Temperature.	Weight.	Mean Temp.	Mean Weight.
92	1145·372}		
99·6	1145·274}	95·8	1145·323
752·4	1138·724}		
753	1138·715}	752·7	1138·720

Therefore expansion for  $180^{\circ} = 0\cdot0128$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot 2606$ .

Expt. XIV.—133·131 grs. of Red Oxide of Manganese in No. 1 Volumenometer :

91·2	696·149}		
98	696·077}	94·6	696·113
753·4	690·654}		
753	690·666}	753·2	690·660

Therefore expansion for  $180^{\circ} = 0\cdot00522$ . Sp. gr. at  $39^{\circ}\cdot 1 = 4\cdot 325$ .

Expt. XV.—424·298 grs. of Sugar Candy, coarsely pounded. No. 3 Volumenometer :

102·6	1048·504}		
111·5	1048·440}	107·0	1048·472
752·6	1042·251}		
755	1042·238}	753·8	1042·244

Therefore expansion for  $180^{\circ} = 0\cdot01116$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot 5927$ .

Expt. XVI.—546·662 grs. of Nitrate of Lead in No. 1 Volumenometer :

99·4	1029·299}		
108·8	1029·261}	104·1	1029·280
753·4	1025·773}		
754·4	1025·771}	753·9	1025·772

Therefore expansion for  $180^{\circ} = 0\cdot00839$ . Sp. gr. at  $39^{\circ}\cdot 1 = 4\cdot 472$ .

The above experiments were, as we have already stated, completed before the commencement of September 1846, and a variety of circumstances prevented our resumption of the research before March in the succeeding year. However, previously to the commencement of the new series, we provided ourselves with a large quantity of turpentine, which after having been well mixed, was decanted into small bottles and preserved over mercury. In this way the turpentine was kept without material change, as will be seen from the following series of results obtained with it before the commencement of the experiments, and after their completion.

**SERIES I. Experiments on the Expansion of Turpentine, on March 20, 1847.**

Volumeno- meter.	Tempe- rature.	Weight.	Mean Tempe- rature.	Mean Weight.	Weight of Bulb.	Weight of Turpentine alone.
No. 1.	89·5	590·119	88·2	590·127	349·546	240·581
	87·0	590·136		584·024	349·546	234·478
	747·6	584·024		747·6	584·024	349·546
No. 2.	89·4	820·472	88·2	820·492	377·036	443·456
	87·0	820·512		809·169	377·036	432·133
	746·6	809·169		746·6	809·169	377·036
No. 3.	89	858·553	88	858·568	397·649	460·918
	87	858·584		847·030	397·649	449·269
	734·1	847·030	739·9	846·918	397·649	449·269
	745·7	846·806		846·918	397·649	449·269

**SERIES II. Experiments on the Expansion of Turpentine, on January 21, 1848.**

Volumeno- meter.	Tempe- rature.	Weight.	Mean Tempe- rature.	Mean Weight.	Weight of Bulb,	Weight of Turpentine alone.
No. 2.	73	820·752	71·5	820·778	377·036	443·742
	70	820·805		809·031	377·036	431·995
	754·6	809·031		754·6	809·031	377·036
No. 3.	754·6	809·032	71·4	809·032	377·036	431·995
	70·8	858·871		858·871	397·649	461·214
	73·2	858·831		858·831	397·649	461·214
	70·2	858·886		858·886	397·649	461·214
	754·6	846·645		846·645	397·649	448·995
	754·6	846·641		846·641	397·649	448·995
	754·6	846·647		846·647	397·649	448·995

In calculating the expansion of the salts, the mean of the above two series was employed, viz. :

Volumenometer.	Temperature.	Weight.	Weight of Volumeno- meter alone.	Weight of Tur- pentine alone.
No. 1.	{ 88·2 747·6	590·127 584·024	349·546 349·546	240·581 234·478
No. 2.	{ 79·85 750·6	820·635 809·100	377·036 377·036	443·599 432·064
No. 3.	{ 79·7 747·25	858·715 846·781	397·649 397·649	461·066 449·132

Exp. XVII.—466·202 grs. of Nitrate of Potash in large crystals.  
No. 3 Volumenometer:

Temperature.	Weight.	Mean Temp.	Mean Weight.
75	1129·601		
78	1129·578}	76·5	1129·589
739·3	1121·954		
746·5	1121·920}	742·9	1121·937

Therefore expansion for  $180^{\circ} = 0\cdot017237$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot 09584$ .

Expt. XVIII.—654·992 grs. of Sulphate of Potash in small crystals, No. 2 Volumenometer:

74·6	1259·066	76·3	1259·060
78·0	1259·054		
738·4	1252·752		
746·6	1252·690		1252·721

Therefore expansion for  $180^{\circ} = 0\cdot010697$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot 65606$ .

Expt. XIX.—302·609 grs. of Copper prepared from the oxide by passing hydrogen gas over it at a red heat. No. 1 Volumenometer:

74	861·271	75·9	861·263
77·8	861·256		
740	855·884		
747·4	855·816		855·850

Therefore expansion for  $180^{\circ} = 0\cdot00767$ . Sp. gr. at  $39^{\circ}\cdot 1 = 8\cdot 41613$ .

Expt. XX.—501·286 grs. of Nitrate of Potash, pounded small. No. 3 Volumenometer:

60	1151·237	61·4	1151·217
62·8	1151·197		
736·6	1143·634		
743	1143·558		1143·596

Therefore expansion for  $180^{\circ} = 0\cdot019487$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot 10657$ .

Expt. XXI.—427·790 grs. of Sulphate of Copper and Ammonia, in large crystals. No. 2 Volumenometer:

60·8	1050·197	62	1050·182
63·2	1050·167		
736	1043·559		
743	1043·499		1043·529

Therefore expansion for  $180^{\circ} = 0\cdot0066113$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot 89378$ .

Expt. XXII.—429·784 grs. of Sulphate of Magnesia and Ammonia, in good crystals. No. 3 Volumenometer:

76·0	1068·645	76·6	1068·644
77·2	1068·643		
739·0	1062·177		
735·6	1062·227		1062·202

Therefore expansion for  $180^{\circ} = 0\cdot007161$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot 71686$ .

Exp<sup>t</sup>. XXIII.—507·958 grs. of Sulphate of Potash and Zinc, in good crystals. No. 2 Volumenometer :

Temperature.	Weight.	Mean Temp.	Mean Weight.
75·0	1129·497		
76·6	1129·463}	75·8	1129·480
738·7	1122·899		
734·5	1122·941}	736·6	1122·920

Therefore expansion for  $180^{\circ} = 0\cdot008235$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot24034$ .

Exp<sup>t</sup>. XXIV.—444·494 grs. of Sulphate of Magnesia and Potash, in good crystals. No. 3 Volumenometer :

75·0	1113·108		
75·8	1113·095}	75·4	1113·101
747·9	1105·678		
748·1	1105·688}	748·0	1105·683

Therefore expansion for  $180^{\circ} = 0\cdot009372$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot05319$ .

Exp<sup>t</sup>. XXV.—456·314 grs. of Sulphate of Copper and Potash, in good crystals. No. 2 Volumenometer :

74·9	1091·772		
75·9	1091·750}	75·4	1091·761
748·3	1084·695		
747·7	1084·701}	748·0	1084·698

Therefore expansion for  $180^{\circ} = 0\cdot009043$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot16376$ .

Exp<sup>t</sup>. XXVI.—449·535 grs. of Sulphate of Copper, in small crystals, prepared by stirring the cupreous solution while cooling. This specimen contained 5·112 equivalents of water, or an excess, due to a mechanical admixture of water. No. 3 Volumenometer.

83·7	1132·089		
84·1	1132·099}	83·9	1132·094
746·2	1124·632		
746·2	1124·674}	746·2	1124·653

Therefore expansion for  $180^{\circ} = 0\cdot005315$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot2422$ .

Exp<sup>t</sup>. XXVII.—320·027 grs. of Sulphate of Ammonia, in fine small crystals. No. 3 Volumenometer :

89·4	1019·9		
81·2	1019·141}	85·3	1019·095
746·2	1011·018		
746·0	1011·005}	746·1	1011·011

Therefore expansion for  $180^{\circ} = 0\cdot010934$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot76147$ .

Exp<sup>t</sup>. XXVIII.—377·686 grs. of Sulphate of Chromium and Potash, in good crystals. No. 2 Volumenometer ;

Temperature.	Weight.	Mean Temp.	Mean Weight.
89·0	1019·481		
81·2	1019·571	85·1	1019·526
746·2	1012·614		
746·2	1012·620	746·2	1012·617

Therefore expansion for  $180^{\circ} = 0\cdot005242$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot85609$ .

Expt. XXIX.—517·725 grs. of Sulphate of Copper, pounded and well pressed between folds of bibulous paper. No. 3 Volumenometer:

86·0	1176·752		
88·0	1176·734	87·0	1176·743
745·3	1169·776		
742·1	1169·812	743·7	1169·794

Therefore expansion for  $180^{\circ} = 0\cdot00812$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot2781$ .

Expt. XXX.—600·594 grs. of Yellow Chromate of Potash, in fine small crystals. No. 2 Volumenometer:

86·0	1227·440		
88·0	1227·427	87·0	1227·433
745·3	1220·612		
742·3	1220·656	743·8	1220·634

Therefore expansion for  $180^{\circ} = 0\cdot011005$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot72309$ .

Expt. XXXI.—467·184 grs. of Potash Alum, in good crystals. No. 2 Volumenometer:

80·0	1053·484		
80·0	1053·480	80·0	1053·482
748·0	1047·995		
744·8	1048·042	746·4	1048·018

Therefore expansion for  $180^{\circ} = 0\cdot003682$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot75125$ .

Expt. XXXII.—402·116 grs. of Binoxalate of Potash, in good crystals. No. 3 Volumenometer:

80·0	1088·032		
80·0	1088·034	80·0	1088·033
748·2	1080·146		
745·0	1080·194	746·6	1080·170

Therefore expansion for  $180^{\circ} = 0\cdot011338$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot04401$ .

Expt. XXXIII.—447·312 grs. of Oxalate of Potash, in good crystals. No. 2 Volumenometer:

61·6	1083·389		
65·0	1083·359	63·3	1083·374
752·2	1075·978		
751·0	1076·014	751·6	1075·996

Therefore expansion for  $180^{\circ} = 0\cdot01162$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot12657$ .

Temperature. Weight. Mean Temp. Mean Weight.

Expt. XXXIV.—406.552 grs. of Chloride of Potassium, coarsely pounded. No. 3 Volumenometer:

60.8	1084.916}	63.2	1084.886
65.6	1084.856}		
752.5	1076.959}	751.9	1076.970
751.3	1076.981}		

Therefore expansion for  $180^{\circ} = 0.010944$ . Sp. gr. at  $39^{\circ}1 = 1.97756$ .

Expt. XXXV.—292.039 grs. of Oxalate of Ammonia, in fine small crystals. No. 3 Volumenometer:

79.2	979.728}	80.8	979.713
82.4	979.698}		
752.0	971.874}	750.9	971.890
749.8	971.907}		

Therefore expansion for  $180^{\circ} = 0.00876$ . Sp. gr. at  $39^{\circ}1 = 1.49985$ .

Expt. XXXVI.—621.193 grs. of Nitrate of Barytes, in small crystals. No. 2 Volumenometer:

85.8	1269.101}	87.9	1269.085
90.0	1269.069}		
745.8	1262.089}	746.4	1262.086
747.0	1262.083}		

Therefore expansion for  $180^{\circ} = 0.004523$ . Sp. gr. at  $39^{\circ}1 = 3.16052$ .

Expt. XXXVII.—450.560 grs. of Bisulphate of Potash, pounded. No. 3 Volumenometer:

86.9	1149.461}	88.5	1149.445
90.1	1149.429}		
746.0	1141.345}	746.5	1141.339
747.0	1141.333}		

Therefore expansion for  $180^{\circ} = 0.012287$ . Sp. gr. at  $39^{\circ}1 = 2.47767$ .

Expt. XXXVIII.—373.783 grs. of Oxalic Acid, in good crystals. No. 2 Volumenometer:

89.2	994.334}	87.8	994.346
86.4	994.359}		
744.9	986.783}	744.8	986.784
744.7	986.785}		

Therefore expansion for  $180^{\circ} = 0.027476$ . Sp. gr. at  $39^{\circ}1 = 1.64138$ .

Expt. XXXIX.—393.044 grs. of Chlorate of Potash, in small crystals. No. 3 Volumenometer:

89.2	1103.259}	87.9	1103.269
86.6	1103.279}		
744.7	1094.718}	744.7	1094.722
744.7	1094.726}		

Therefore expansion for  $180^{\circ} = 0.017112$ . Sp. gr. at  $39^{\circ}1 = 2.32643$ .

Exp<sup>t</sup>. XL.—541·833 grs. of Chloride of Barium, in small crystals.  
No. 2 Volumenometer :

Temperature.	Weight.	Mean Temp.	Mean Weight.
64·8	1206·826	67·1	1206·800
69·4	1206·774		
755·4	1198·800	755·8	1198·797
756·2	1198·794		

Therefore expansion for  $180^{\circ} = 0\cdot009873$ . Sp. gr. at  $39^{\circ}\cdot 1 = 3\cdot 05435$ .

Exp<sup>t</sup>. XLI.—326·462 grs. of Sugar of Milk, pounded. No. 3 Volumenometer :

65·0	998·393	67·2	998·383
69·4	998·373		
755·6	990·721	755·9	990·720
756·2	990·719		

Therefore expansion for  $180^{\circ} = 0\cdot009111$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot 53398$ .

Exp<sup>t</sup>. XLII.—307·866 grs. of Binoxalate of Ammonia in good crystals. No. 2 Volumenometer :

81·8	960·874	83·6	960·862
85·4	960·850		
750·8	953·203	750·9	953·210
751·0	953·217		

Therefore expansion for  $180^{\circ} = 0\cdot013718$  sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot 61341$ .

Exp<sup>t</sup>. XLIII.—234·865 grs. of Bichromate of Chloride of Potassium in good crystals. No. 3 Volumenometer :

81·6	1010·939	83·4	1010·914
85·2	1010·889		
750·7	1000·808	750·9	1000·816
751·1	1000·824		

Therefore expansion for  $180^{\circ} = 0\cdot015902$ . Sp. gr. at  $39^{\circ}\cdot 1 = 2\cdot 49702$ .

Exp<sup>t</sup>. XLIV.—392·901 grs. of Quadroxalate of Potash in good crystals. No. 2 Volumenometer :

74·5	1026·945	75·3	1026·940
76·1	1026·935		
751·0	1019·509	752·2	1019·502
753·4	1019·494		

Therefore expansion for  $180^{\circ} = 0\cdot015916$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot 84883$ .

Exp<sup>t</sup>. XLV.—396·646 grs. of Quadroxalate of Ammonia in good crystals. No. 3 Volumenometer :

74·9	1044·521	75·6	1044·518
76·3	1044·515		
751·0	1037·270	752·2	1037·263
753·4	1037·256		

Therefore expansion for  $180^{\circ} = 0\cdot014347$ . Sp. gr. at  $39^{\circ}\cdot 1 = 1\cdot 65194$ .

The foregoing results are collated in the following Table :

No. of Exp.	Name of Salt.	Formula.	Atomic weight.	Expansion for 18°.	Sp. gravity at 39°.1.	Atomic Volume.	Atomic Volume, divided by 1.225.
11	Copper	Cu	31.66	0.0055 ditto	8.367 8.41613	3.7839 3.7618	3.0889 3.0709
19	Ditto	HgO	108.07	0.005802 ditto	11.136 9.7046	7.9221 7.9221	7.9221
1	Red Oxide of Mercury	PbO	111.56	0.00795 ditto	9.3634 11.78	9.7037 9.7037	9.7037
8	Protioxide of Lead	Mn <sub>3</sub> O <sub>4</sub>	115.9	0.00522 ditto	4.325 4.325	21.706 21.706	21.706
14	Red Oxide of Manganese	Sn O <sub>2</sub>	74.82	0.00172 ditto	6.7122 6.7122	11.147 11.147	9.0995 9.0995
5	Peroxide of Tin	Ph <sub>2</sub> S	119.56	0.01045 ditto	6.9238 7.45	17.268 19.096	14.096 14.096
2	Sulphuret of Lead	K Cl	74.5	0.010944 ditto	1.97756 1.97756	37.673 37.673	30.753 30.753
34	Chloride of Potassium	Ba Cl + 2HO	122.14	0.009873 ditto	3.05435 3.05435	39.989 39.989	32.644 32.644
40	Chloride of Barium	NH <sub>4</sub> Cl	53.5	0.0191 ditto	1.5333 1.5333	34.892 34.892	28.483 28.483
4	Chloride of Ammonium	NaO <sub>2</sub> NO <sub>3</sub>	85.0	0.0128 ditto	2.2606 2.2606	37.601 37.601	30.694 30.694
13	Nitrate of Soda	KO <sub>2</sub> NO <sub>3</sub>	101.0	0.01967 ditto	2.1078 2.09584	47.917 48.191	39.116 39.339
10	Nitrate of Potash	ditto	17	0.017237 ditto	2.09584 2.10657	39.339 47.945	39.339 39.139
17	Ditto	ditto	20	0.019487 ditto	4.472 4.472	37.021 37.021	37.021 37.021
20	Nitrate of Lead	PbO <sub>2</sub> NO <sub>3</sub>	165.56	0.00839 ditto	3.16052 3.16052	41.335 41.335	33.743 33.743
16	Nitrate of Barytes	BaO <sub>2</sub> NO <sub>3</sub>	130.64	0.004523 ditto	2.32643 2.32643	52.656 52.656	42.984 42.984
36	Chlorate of Potash	KO <sub>2</sub> ClO <sub>3</sub>	122.5	0.017112 ditto	0.01134 0.01134	2.711 2.711	36.573 36.573
39	Chromate of Potash	KO <sub>2</sub> Cr O <sub>3</sub>	99.15	0.01134 ditto	0.011005 0.01122	2.72309 2.692	29.866 29.723
12	Chromate of Potash	ditto	30	0.01122 ditto	151.3 178.8	36.411 56.204	36.411 45.880
30	Ditto	KO <sub>2</sub> 2Cr O <sub>3</sub>	178.8	0.015902 ditto	2.49702 1.64138	71.605 38.382	58.453 31.332
3	Bichromate of Potash	K Cl + 2Cr O <sub>3</sub>	63.0	0.027476 ditto	2.12657 0.01162	43.262 43.262	35.316 35.316
43	Bichromate of Potassium	HO <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + 2HO	92.0	0.01162 ditto	92.0	2.12657	35.316 35.316
38	Oxalic Acid	ditto	33	0.01162 ditto	92.0	2.12657	35.316 35.316
33	Oxalate of Potash	ditto					

No. of Exp.	Name of Salt.	Formula.	Atomic weight.	Expansion for 18° <sup>o</sup>	Sp. gravity at 39°.1.	Atomic Volume.	Atomic Volume, divided by 1.225.
32	Binoxalate of Potash . . . . .	KO, $2C_2O_4 + 3HO$	146.0	0.011328	2.04401	58.309	
44	Quadroxalate of Potash . . . . .	KO, $4C_2O_4 + 7HO$	254.0	0.015916	1.84883	112.150	
35	Oxalate of Ammonia . . . . .	NH <sub>4</sub> O, $C_2O_4 + HO$	71.0	0.00876	1.49985	47.338	38.643
42	Binoxalate of Ammonia . . . . .	NH <sub>4</sub> O, $2C_2O_4 + 3HO$	125.0	0.013718	1.61341	77.476	63.245
45	Quadroxalate of Ammonia . . . . .	NH <sub>4</sub> O, $4C_2O_4 + 7HO$	233.0	0.014347	1.65194	141.046	115.140
18	Sulphate of Potash . . . . .	KO, SO <sub>4</sub>	87.0	0.010697	2.65666	32.755	
37	Bisulphate of Potash . . . . .	KO, SO <sub>3</sub> + HO, SO <sub>3</sub>	136.0	0.012287	2.47767	54.890	44.808
27	Sulphate of Ammonia . . . . .	NH <sub>4</sub> O, SO <sub>3</sub> + HO	75.0	0.010934	1.76147	42.578	34.758
7	Sulphate of Copper . . . . .	CuO, SO <sub>3</sub> + 5HO	124.66	0.009525	2.2901	54.434	44.436
26	Ditto . . . . .	ditto	0.005315	2.24422	55.597		
29	Ditto . . . . .	ditto	0.008112	2.2781	54.721	44.670	
6	Sulphate of Iron . . . . .	Fe O, SO <sub>3</sub> + 7HO	139.0	0.01153	1.8889	73.588	60.072
9	Sulphate of Magnesia . . . . .	MgO, SO <sub>3</sub> + 7HO	123.67	0.01019	1.6829	73.486	59.989
21	Sulphate of Copper and Ammonia . . . . .	CuO, SO <sub>3</sub> + NH <sub>4</sub> O, SO <sub>3</sub> + 6HO	199.66	0.0066113	1.893378	105.430	86.065
25	Sulphate of Copper and Potash . . . . .	CuO, SO <sub>3</sub> + KO, SO <sub>3</sub> + 6HO	220.66	0.009043	2.16376	101.980	83.249
24	Sulphate of Magnesia and Potash . . . . .	MgO, SO <sub>3</sub> + KO, SO <sub>3</sub> + 6HO	201.67	0.009372	2.05319	98.223	80.182
28	Sulphate of Chromium and Potash . . . . .	Cr <sub>2</sub> O <sub>3</sub> , 3SO <sub>3</sub> + KO, SO <sub>3</sub> + 24HO	503.3	0.005242	1.85609	271.161	221.356
31	Potash Alum . . . . .	Al <sub>2</sub> O <sub>3</sub> , 3SO <sub>3</sub> + KO, SO <sub>3</sub> + 24HO	476.38	0.003682	1.75125	272.023	222.060
23	Sulphate of Potash and Zinc . . . . .	ZnO, SO <sub>3</sub> + KO, SO <sub>3</sub> + 6HO	221.0	0.008235	2.24034	98.646	80.527
22	Sulphate of Magnesia and Ammonia . . . . .	MgO, SO <sub>3</sub> + NH <sub>4</sub> O, SO <sub>3</sub> + 6HO	180.67	0.007161	1.71686	105.233	85.904
15	Cane Sugar . . . . .	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	171.0	0.011160	1.3921	107.365	87.645
41	Sugar of Milk . . . . .	C <sub>12</sub> H <sub>22</sub> O <sub>12</sub>	180.0	0.009111	1.33398	117.342	95.789

On a cursory inspection of the above table, it will be observed that considerable discrepancy occurs in the results obtained with salts of the same name. This must not throw doubt on the accuracy of the experiments, as it arose from the state in which the salts were tried. The specific gravity of copper in the 19th experiment is somewhat greater than that in the 11th experiment; the reason for which is, that the copper in the former case was exposed to hydrogen at a red heat for a considerable time after the oxygen had been removed from the oxide. In the case of nitrate of potash, the 17th experiment was made with large crystals, averaging  $\frac{1}{16}$  of an inch in diameter, whilst in experiment 20 we employed another portion of the same salt pounded very small, so as to free it from mechanical water, and in experiment 10 a different specimen was used in small crystals. It will be observed, that a very considerable difference exists between the results of the three trials. The large crystals were lighter and in a more coerced state, as shown by their smaller expansion. Of the three specimens of sulphate of copper tried, that employed in experiment 26 had, as we have stated, a larger quantity of water than 5 equivalents attached to it, and hence we observe a great difference in its expansion and specific gravity, the decrease of gravity being, as before, accompanied by a decrease of expansion. With regard to the expansions, we may call attention to the close approximation of the highly hydrated salts to 0·01125, or the expansion of ice as determined by Brunner. The expansion of oxalic acid is remarkable as being greater, and that of peroxide of tin as being less than those of any solid bodies on record. In all cases of hydrated salts, it is extremely difficult to obtain them in their exact normal state of hydration, and therefore the results of experiment with different specimens are subject to variation.

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XIII.—*On the disappearance of the Volume of the Acid, and in some cases of the Volume of the Base, in the Crystals of highly hydrated Salts. By LYON PLAYFAIR, F.R.S., and J. P. JOULE.*

RESEARCHES ON ATOMIC VOLUME.—SERIES V.

WE have had the honour to present to the Society several Memoirs on the Atomic Volumes of Salts. In the first of these, we pointed out three distinct facts, with reference to hydrated salts, which increased experience has only the more confirmed us in believing to be strictly true.

1st. That the anhydrous portion of highly hydrated salts, when dissolved in water, occupies no space, if allowance be made for the increased expansibility of the solution.

2nd. That the hydrated salts of one class take up, in their solid state, the space which would be occupied by their water frozen into ice, the volume of their anhydrous portion ceasing to be recognised.

3rd. That hydrated salts of a second class take up the space represented by the number of their equivalents of water multiplied by the empirical number 11, instead of 9·8, which latter number represents the volume of ice.

In our first Memoir, we fully admitted that the empirical number 11 was merely an approximation to the truth; and in our second communication, we shewed that it was more strictly  $9\cdot8 + \frac{9\cdot8}{8} = 11\cdot025$ .

The number 9·8, assumed for the volume of ice, is derived from that denoting the specific gravity of that body, which our experiments shewed to be 0·9184, a result almost identical with the number 0·918 as determined by Brunner.

Two classes of objections have been made to our researches. The first by Berzelius and others, that the methods which we employed for obtaining the specific gravity were not likely to be very accurate. Although fully confident of their general accuracy, we considered it due to criticism, generally so just as that of this philosopher, to repeat all our experiments with the greatest care, not with new instruments such as those we had previously used, but by processes universally recognised. In the previous paper, we have done this with much labour, and at the same time elicited the influence of temperature on specific gravity, but without obtaining results in any degree materially different, or nearer to theory than were obtained with the apparatus formerly used. Our new experiments are contained in the Memoir just read to the Society.

A second class of objectors urged that no rule was given when the volume 9·8, should be taken and when the volume 11·0. This objection was perfectly just, and was always entertained by ourselves. We stated in our first Memoir,\* "That for the present, we announce the number 11 empirically," as being an expression of experiment not as being its rational exposition. Future research alone could explain the cause of this number, and to its elucidation we have devoted ourselves. In our second Memoir, we endeavoured to show that this number 11 was itself a multiple of a number,  $\frac{9\cdot8}{8} = 1\cdot225$ , at least in the case of a large number of bodies, and we now proceed to point out how it is that in the hydrated salts, this number so frequently appears as the expression of experiment. We take one class of salts at a time, because the deliberate study of one is

\* Memoirs of the Chemical Society, vol. II. p. 477.

better calculated to lead us to truth, and enable us to abandon error. In pursuance of our plan, this Memoir is confined to hydrated salts only.

In the first place, we call attention to the fact already noticed in our first Memoir, that there are certain hydrated salts, in which the water alone takes up space in the solid state. The specific gravities of these had already been frequently determined, our results agreeing closely with those of former experimentalists. We therefore adduce the table given on a former occasion, no further experiments having been made.

TABLE I.

DESIGNATION.			VOLUME IN SALT.					Specific gravity by experiment.
Name.	Formula.	Atomic weight.	Volume of salt by experiment.	98, or volume of ice as unity.	Volume by theory.	Sp. gr. by theory.		
Carbonate of Soda	Na O, CO <sub>2</sub> + 10 HO	143·4	98·6	10	98·0	1·463	1·454	
Phosphate of Soda	2 Na O, HO, PO <sub>5</sub> + 24 HO	359·1	235·5	24	235·2	1·527	1·525	
Sub-phosphate of Soda	3 Na O, PO <sub>5</sub> + 24 HO	381·6	235·2	24	235·2	1·622	1·622	
Arseniate of Soda	HO, 2 Na O, As O <sub>5</sub> + 24 HO	402·9	232·0	24	235·2	1·713	1·736	
Sub-arseniate of Soda	3 Na O, As O <sub>5</sub> + 24 HO	425·2	235·6	24	235·2	1·808	1·804	

Cane-sugar is a remarkable example of this class, as showing that the hydrogen and oxygen are present *quasi* water, the carbon occupying no space. It was interesting to test this with milk-sugar, the specific gravity of which we had carefully determined in the preceding paper. The following table proves that in the two cases of cane-sugar and sugar-of-milk, the carbon ceases to occupy space, and the water takes up the exact volume which it should do if it were frozen into ice.

TABLE II.

	Formula.	Atomic weight.	Volume by theory, supposing the HO to take the space of ice.	Specific gravity by Theory.	Volume by Experiment.	Specific gravity by Experiment.
Cane Sugar	C <sub>12</sub> H <sub>11</sub> O <sub>11</sub>	171	107·8	1·586	107·4	1·593
Milk Sugar	C <sub>24</sub> H <sub>24</sub> O <sub>24</sub>	360	235·2	1·531	234·7	1·534

The specific gravity of cane-sugar according to other experimentalists, is 1·606 by Musschenbröck, 1·600 and 1·585 by Schübler and Renz ; and of milk-sugar, 1·548 by Schübler.

The coincidence between the observed and calculated numbers, in the above two tables, is so striking, as to leave no doubt that both the acid and base of the salts and the carbon of the sugars\* cease to occupy space, having merged into the volume of the water. In these tables there is nothing new beyond the addition of milk-sugar to the series, the general fact having been enunciated in our first Memoir.

We now direct attention to the hydrated salts, possessing a larger volume than that due to the water contained in them ; that is, to those salts in which the factor, representing the number of atoms of water, had to be multiplied by 11 instead of by 9·8.

Table III is constructed upon two assumptions ; first, that the water, as in other hydrated salts, takes up the space of ice, and, second, that the base takes up the same space in the hydrated as it does in the anhydrous salt. These two assumptions being admitted, the sum of the volumes of the solid water and of the base is exactly equal to the total volume of the salt, *nothing being left for the acid, which therefore has ceased to occupy space.* This result being very remarkable, it is necessary to examine closely into the evidence on which it rests. It has been shewn in our Second Memoir, that the volumes of the protoxides of copper, zinc, magnesia, nickel and iron in combination are 6·12, which is also the volume of the oxides in their state of greatest density when separated. The experimental volume of the sulphates of these oxides is as a mean 22·17,† which is very near the theoretical number 22·05.‡ The volume of sulphuric acid being 15·92, the difference 6·12 leads to the same theoretical result, as that obtained for the oxides in their densest state. If instead of this theoretical number, that procured by experiment were substituted, the difference would only be in the decimal place and not affect the general accordance of the above table.

The volume of soda in its salts is derived from the mean specific gravity 2·562 for sulphate of soda, as determined by various experimentalists, (2·46 Mohs., 2·631 Karsten, 2·597 P. and J.) This mean result gives 27·9 for the volume of sulphate of soda, from which must be deducted 15·9, the known volume of sulphuric acid, leaving 12 as the volume for soda ; the theoretical result is 12·25.§

\* We have not estimated the sp. gr. of grape-sugar. Guerin states it to be 1·386, which would appear to make it belong to a different class, as the sp. gr. necessary to give it the volume due to its solid water only, would be 1·442.

† Chem. Mem. vol. I. p. 433.

‡ Idem, vol. II. p. 101.

§ The volume of soda when separate, so far as we may rely on one experiment, that of Karsten, is 11·0 instead of 12·2.

TABLE III.

Salts.	Formula.	Atomic weight.	Space occupied by solid water.	Space occupied by base.	Sum of spaces occupied by base and water.	Theoretical sp. gr.	Vol. of Sp. gr. salt by exp.	Specific gravity by various authorities.
Sulphate of Copper	Cu O, SO <sub>3</sub> + 5 HO	124.66	49.00	6.12	55.12	2.261	54.7	2.279 { 2.284, P. and J. 2.274, Kopp.
Sulphate of Zinc	Zn O, SO <sub>3</sub> + 7 HO	143.43	68.6	6.12	74.72	1.919	74.2	1.931 { 1.90, Musschenbroeck. 1.912, Hassenfratz.
Sulphate of Magnesia	Mg O, SO <sub>3</sub> + 7 HO	123.67	68.6	6.12	74.72	1.655	73.5	1.660, Hassenfratz. 1.674, Kopp. 1.680, P. and J.
Sulphate of Iron	Fe O, SO <sub>3</sub> + 7 HO	139.0	68.6	6.12	74.72	1.860	73.58	1.888 { 1.84, Hassenfratz. 1.88, Musschenbroeck.
Sulphate of Nickel	Ni O, SO <sub>3</sub> + 6 HO	131.74	58.8	6.12	64.92	2.029	64.6	2.037 { 2.037, Kopp. 1.470, Leonhard.
Sulphate of Soda	Na O, SO <sub>3</sub> + 10 HO	161.48	98.0	12.25	110.25	1.464	109.9	1.469 { 1.481, Mohs. 1.380, Watson.
Sulphate of Alumina	Al <sub>2</sub> O <sub>3</sub> , 3 SO <sub>3</sub> + 18 HO	333.7	176.4	22.05	198.45	1.681	199.6	1.671 1.720, Musschenbroeck.
Biborate of Soda	Na O, 2 BO <sub>3</sub> + 10 HO	191.23	98.0	12.25	110.25	1.734	110.5	1.730 { 1.723, Hassenfratz. 1.740, Kirwan.
Pyrophosphate of Soda - 2 Na O, PO <sub>5</sub> + 10 HO	224.15	98.0	24.50	122.50	1.829	122.0	1.836 { 1.716, Mohs. 1.740, Accum. 1.905, Turner mann.	

The volumes of all the oxides in the table, except alumina, are therefore derived from experiment, but in the latter case we are obliged to make an assumption. The specific gravity of ignited alumina is known, but not of alumina as it exists in its salts. In order to arrive at its volume, it is necessary to compare it with what we know of other oxides. Now we are aware that in the sesquioxides, oxygen frequently takes up the volume  $1 \cdot 225 \times 3$ , or  $3 \cdot 675$ . Wohler gives 2·5 as the sp. gr. of aluminium, and 2·67 as the result of another estimation. The first estimation, in giving the same volume to aluminium as to chromium in its least dense state, has analogy in its favour, and the volume calculated from it would be 5·47, which is not far from theory, the latter affording 5·51. The volume of alumina in its least dense form would, therefore, be  $5 \cdot 51 \times 2 + 3 \cdot 675 \times 3 = 22 \cdot 04$ . This number then, though strengthened by analogy, is only an assumption, and must be distinguished as such from the experimental facts above recorded.

It is now important to extend our evidence to another class of highly hydrated salts, and in these it will also be seen that the acid ceases to occupy appreciable space. The alums offer a good series of salts for testing this view, but from our ignorance of the specific gravity of their bases before calcination, certain assumptions have to be made with regard to their volumes. It is well known that alumina, oxide of chromium, and peroxide of iron contract amazingly when heated, so that the bulk of the calcined oxides by no means denotes that of the base in combination.

In the class of the alums, we assume, for reasons formerly given, that alumina has the volume 22·05. Chromium in its least dense form has, according to Thomson, the sp. gr. 5·10, or a volume of 5·5, the same as that found for aluminium; its corresponding oxide will therefore have a volume in its salts of 22·05. With respect to iron alum, the assumption is made, which is only justified by its isomorphism, that the volume of peroxide of iron in its salts is equal to that of the oxide of chromium and that of alumina in their respective salts; it must be remembered, however, that in the isolated state we do not know this oxide to have a higher volume than 17·15. Potash has a volume of 17·75, according to the specific gravity of Karsten (2.756), which does not differ much from the volume deduced from the sulphate, viz.: 17·1. The volume of anhydrous sulphate of ammonia is 39·2 by experiment,\* from which 15·9 being deducted for sulphuric acid, 23·3 is left as the volume of the oxide of ammonium in the sulphate.

\* Vol. I. Chem. Mem. p. 428.

TABLE IV.

Name.	Formula.	Atomic weight.	Vol. of solid water.	Vol. of proper metallic base.	Sum of vol. of water and bases.	Theoretical sp. gr.	Vol. by exp.	Sp. gr. by mean exp.	Various authorities.
Potash Alum .	$\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 + \text{K}_2\text{O} \cdot \text{SO}_3 + 24\text{HO}$	476.38	235.2	22.05	17.15	27.4	1.736	274.0	1.731
Ammonia Alum .	$\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 + \text{NH}_4\text{SO}_3 + 24\text{HO}$	455.38	235.2	22.05	23.27	280.52	1.623	280.2	1.625
Chrome Alum .	$\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot \text{K}_2\text{O} \cdot \text{SO}_3 + 24\text{HO}$	503.3	235.2	22.05	17.15	27.4	1.834	273.1	1.843
Ammonia Iron Alum	$\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot \text{NH}_4\text{O} \cdot \text{SO}_3 + 24\text{HO}$	481.03	235.2	22.05	23.27	280.52	1.714	280.5	1.715

The assumption in this table is in the case of peroxide of iron; but this being admitted, no other conclusion can be drawn from it than that, in the class of alums, *the water takes up the space which it would do if frozen into ice, the bases assume their own proper volumes, the 4 equivalents of acid occupying no appreciable space.* If we refuse all assumption in this class of alums, and suppose the metallic sesquioxides in combination to have the volume of their ignited oxides (17·15), there would still be only 4·89 left for 4 equivalents of sulphuric acid, which ought to take up the volume of 63·6; it is therefore certain that at least 3½ equivalents of acid have disappeared.

It is unnecessary to tabulate the volumes of the double sulphates of copper, zinc, magnesia, iron and nickel, with the sulphates of potash and ammonia, the following list giving sufficient information for our present purpose.

	Atomic weight.	Sp. gr. by exp <sup>t.</sup>	Atomic vol. by exp <sup>t.</sup>
Sulphate of Copper and Potash . . .	220·66	2·163*	102·0
"    "    " Ammonia . . .	199·66	1·893	105·4
"    "    " Zinc and Potash . . .	221·0	2·240	98·6
"    "    " Ammonia . . .	200·0	1·897	105·4
"    "    " Magnesia and Potash . . .	201·67	2·053	98·2
"    "    " Ammonia . . .	180·67	1·717	105·2
"    "    " Iron and Potash . . .	216·73	2·202	98·4
"    "    " Ammonia . . .	195·5	1·848	105·8

The average volume of the double potash salts, as deduced from the above table, is 99·3, including the copper salt, which appears to be an exception to the rule. The other salts, excluding this, have a volume of 98·4. The average volume of the double ammonia salts is 105·4. The general formula of the potash salts is RO, SO<sub>3</sub>+KO, SO<sub>3</sub>+6HO. We have already shewn that the volume best representing that of the magnesian oxides in combination is 6·125, and the volume of sulphate of potash by experiment is 33·075.

$$6 \text{ eq. Water} = 9\cdot8 \times 6 = 58\cdot8$$

$$1 \text{ eq. Magnesian oxide} = 6\cdot125$$

$$1 \text{ eq. Sulphate of Potash} = 33\cdot075$$

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$$98\cdot000$$

If therefore we except sulphate of copper and potash, which

\* We here give the result obtained with great care as described in the preceding paper, although it differs considerably from that formerly obtained, 2·244.

perhaps from containing mechanical water may have given a specific gravity lower than the truth, we find that the double salts are made up of the volumes of their constituents, the sulphuric acid of the magnesian salt having ceased to occupy space.

The ammoniacal sulphates are made up in the same way.

6 eq. Solid Water . . . . =	58·8
1 eq. Magnesian oxide . . . =	6·125
1 eq. Sulphate of Ammonia =	39·2

104·12

There are probably other hydrated salts, which might be included among those treated in this paper, but we are anxious at present not to complicate the question, having selected those whose sp. gr. may be considered well established. We now sum up the preceding observations as follows :

1. The water in highly hydrated salts always occupies the volume of ice.

a. In the class of hydrated arseniates and phosphates with 24 atoms of water, neither acid nor base occupy space, the volume of the solid water alone accounting for that of the salt.

b. In cane and milk sugar the carbon ceases to occupy space.

2. Another class of salts, including all the hydrated magnesian sulphates, sulphate of alumina, borax, pyrophosphate of soda, and the alums, possess a volume made up of that of their bases and of their solid water, their acids ceasing to be recognisable in space.

Attention has now to be drawn to some points, which at present we introduce incidentally, without giving them the character of a substantive law, rather looking upon them in the light of coincidences.

We have already viewed the volumes of bodies as being the multiples of  $\frac{9\cdot8}{8}$  or of 1·225. We gave reasons for taking this as a standard unit, and not merely as an arbitrary number for comparison. The consideration of the previous tables now leads to the remarkable result, that, speaking generally, there is one atom of constitutional\* water added for every unit volume existing in the base. Thus the constitutional water of the magnesian sulphates amounts to five atoms. The two additional atoms present in certain cases being lost in dry air. The volume of the base of these oxides is  $1.225 \times 5$ . Again, there are 18 atoms of

\* The term *constitutional water* applied here refers to the water of crystallization, and not to that to which the same name is applied by Graham.

water in sulphate of alumina, the oxide itself having a volume of  $1\cdot225 \times 18$ . Sulphate of soda affects 10 atoms of water, and soda enjoys a volume of  $1\cdot225 \times 10$ . Borate of soda also possesses 10 atoms of water. It is this circumstance, be it accidental or otherwise, which led to the result, that in many cases, the volume of a hydrated salt is the number of its atoms of water multiplied by 11; the number 9·8, the true volume of solid water, being so generally associated with the unit volume 1·225 of the base, and the sum of these giving the number 11·025. There are exceptions to this, which prevent it being announced as general, even in this limited class of salts. The pyrophosphate of soda, containing 2 atoms of soda, possesses only 10 atoms of water, although it might have had 20. The potash of the sulphate of potash in alum has not the number of atoms of water added to it corresponding to its unit volumes, although its acid ceases to occupy space.

In the first class of hydrated salts, there is one atom of water added for every unit volume of their *acid*. Thus phosphoric acid and arsenic acid both affect a volume of  $1\cdot225 \times 24$ , and the atoms of water attached to their salts are also 24 in number; but in this case the volumes, both of the base and the acids, are merged.

This, however, cannot be looked upon in any other light than as fortuitous; because, in the carbonate of soda belonging to this series, carbonic acids affect only 9 of their unit volumes, though in the carbonates of potash it has 110 unit volumes. Another fact, which, on account of the limited class of salts examined, may be altogether accidental, is, that the number of atoms of water attached to the salts in Table I is exactly double the number of ultimate atoms in the anhydrous salt. Thus there are 12 anhydrous atoms in the phosphates and arseniates, and 24 atoms of water; in carbonate of soda, there are 5 anhydrous atoms and 10 atoms of water. It is impossible to avoid the speculation that the attachment of atoms of water to the magnesian sulphates, in some such manner as in the class of phosphates, may be the cause of the volume of their bases disappearing when these salts are dissolved in water.

The undoubted result of the disappearance of the volume of the acid is of much importance in considering the constitution of hydrated salts. By this disappearance we should be led to suppose, that the water and the acid in hydrated salts are in more intimate union than the acid and base; in other words, that the salt was rather water and acid+base, than acid and base+water. Looking back to the results in this point of view, the constitutional water added to the sulphuric acid of all the sulphates examined, except

sulphate of soda, amounts to 6 atoms, allowing that the magnesian oxide plays the part of water, as it so often does. Thus then, we have  $\text{RO}$ ,  $5\text{HO}$ ,  $\text{SO}_3$  in the sulphates of the magnesian class ; in the alums we have  $4(6\text{HO}, \text{SO}_3) + \text{Al}_2\text{O}_3 + \text{KO}$ .

In the case of sulphates of zinc, magnesia and iron, there is a disposition to affect seven atoms of water, and we find their radicals also inclined under certain circumstances to affect larger volumes than others. Thus magnesium has a volume of 5.5 ; iron in the alums has also a similar volume, and zinc usually possesses a volume of 4.9, instead of 3.12.

It may be merely a coincidence that the number of unit volumes in the base corresponds to that of the number of atoms of the water, for we possess few other salts upon which we can test this view ; but on the doctrine of probabilities the wager is a high one against it being merely chance. It accounts, however, sufficiently for our having supposed that water in combination possessed the volume 11. We now withdraw that opinion, having convinced ourselves by the previous study, *that in all the cases mentioned in this paper, the water attached to salts has exactly the volume of ice.*

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### Anniversary Meeting, March 30, 1848.

The President in the Chair.

The following Annual Report of the Council was read by the President.

In reviewing the Proceedings of the Chemical Society of London during the past year, the seventh namely of its existence, your Council sees with satisfaction that there is an increase in the number of its Members. It is now constituted of 102 Resident Members, 106 Non-resident Members, 7 Associates, and 9 Foreign Members, making a total of 224 Members, and producing an annual income of £300. In the course of the past year 25 new Members have been elected, namely : 15 Resident and 7 Non-resident Members ; 1 Associate and 2 Foreign Members, namely : Dr. Kolbe of Brunswick, and M. Dumas of Paris.

During the past year the Society has lost, by death, 1 Resident and 4 Non-resident members, namely : Mr. Charles Askin, of Birmingham ; Mr. David Mushet, of Coleford ; Mr. Thomas Starkie Thomson, of Clitheroe ; Mr. Francis Watkins, of London, Optician ; Mr. John Wilson, of the Hurlet Alum Works, near Paisley.

Mr. Askin was born at Cheadle in Staffordshire. He was brought up to the business of a draper and succeeded to the establishment of his father. He early manifested an ardent interest in the pursuits of science,

especially of Physics and Chemistry; and soon received from his fellow-townsman the appellation of "Schemer." Having relinquished his business, he qualified himself by study in London as a veterinary surgeon, in which capacity he practised for some years in Birmingham, but soon grew tired of his adopted profession, and entered into a contract with a Mining Company to proceed to Mexico to take the management of amalgamation works. But, previously, he determined to acquire an extensive practical knowledge of metallurgy, and, with that view, visited various metallurgical works both in this country and on the continent, especially those of Freiburg in Saxony. On his return, he passed through Warsaw, where he remained for some time at the house of his friends, the Messrs. Evans, proprietors of extensive iron works in that city. One day as he was strolling through the street, his attention was accidentally directed to some articles of the so-called *German silver* exhibited in a shop-window, and he immediately expressed an opinion that that alloy, which was then comparatively novel, might be produced of superior quality, and that the refining of nickel might become an important and lucrative manufacture. From that time he resolved to devote his energies to the subject. On his arrival in England he obtained a release from his Mexican engagement, and set himself vigorously to the work of refining Nickel by the "Wet Way." After much persevering application, and many fruitless experiments, he finally succeeded in accomplishing his object to his entire satisfaction. The result of his labours is, that in Birmingham there are now extensive nickel-works, in which the metal is manufactured in a state of almost chemical purity. It is only a few years ago that Mr. Askin discovered a practical method of separating nickel from cobalt on the large scale; and Birmingham now supplies the principal potteries of this country, as well as several in France including the celebrated works of Sèvres, with oxide of cobalt in a state of purity such as was formerly unknown. The beauty of tint of the recent blue earthenware is entirely due to the *purity* of the oxide of cobalt employed. By this discovery, the price of cobalt has not only been considerably reduced, but Mr. Askin himself realized an ample fortune. He had made arrangements for retiring from business, when death most unexpectedly closed his career on the 25th of August 1847, in the secluded valley of Grisdal, amidst the mountains of Norway, whither he had accompanied his partner, Mr. Evans, partly for the sake of recreation, and partly with the view of giving his advice concerning some melting works then in process of erection. The intelligence of his decease, which occurred in the fifty-ninth year of his age, was received by a large circle of friends with feelings of sincere sorrow.

Mr. David Mushet was born in 1773, at Dalkeith, near Edinburgh, where he also received his education. At an early age he became an accountant at the Clyde Iron Works. Finding how little was really practically known upon the important subject of the reduction of iron ore, and how unsatisfactory and imperfect the whole *theory* of the process

was, he determined upon undertaking a series of experimental inquiries, with a view to its elucidation. In this praiseworthy resolution he persevered under numerous obstacles which would have damped the ardour of a less energetic mind, and succeeded, not merely in shewing the nature of the mutual actions which ensue between the fluxes and the ores and the cause of the various qualities of the varieties of cast iron, but in introducing extensive practical improvements into every branch of that vast manufacture. Amongst these his discovery, in 1801, of the value and mode of working what has been termed the *Black-band-iron stone*, stands pre-eminent. He was at that time engaged in erecting the Calder Iron Works, and it appears from his own memorandum, that the greatest prejudice was excited against him by the iron masters of the day for presuming to class what were termed the *wild coals* of the country with iron stones fit and proper for the blast furnace. This discovery tended to elevate Scotland to a considerable rank amongst the iron-making nations of Europe, and to show that resources are still in store, apparently inexhaustible. But although Mr. Mushet was, to use his own phrase, long regarded as the intrusive visionary of the laboratory, he fortunately lived to see a more rational estimate, and grateful acknowledgment of the value of his labours. "Time," as Lord Bacon says, "is a great innovator," but it was not till after a period of nearly forty years that he reaped this soothing consolation. He very truly observes, that there are many, very many, to whom even such tardy measures of justice have been in their lifetime entirely denied. Mr. Mushet is represented by those who knew him to have been a straight-forward and well-informed man; his habits were, what are usually termed, of the old school, he was frugal, industrious and punctual. The expenses of a large family prevented his amassing wealth, but he was in the receipt of a considerable income, which was the fruit of his own diligence and perseverance. He died at Monmouth in the month of June, 1847, at the age of 74.

Besides many valuable contributions to Encyclopædias and Journals, Mr. Mushet published in the Philosophical Magazine, an extensive series of papers, practical and experimental upon iron and steel, which have been collected and republished, with copious illustrative notes, forming a bulky 8vo. volume, printed in 1840. The article "Iron" in Napier's Supplement to the Encyclopædia Britannica, and the articles "Blowing Machine" and "Blast Furnace" in Rees' Cyclopædia, are by Mr. Mushet.

Mr. Thomas Starkie Thomson was born at Primrose, near Clitheroe, in the year 1811, and after passing through the ordinary routine of a Grammar-school education there, was removed to Manchester, where he acquired, under the late Mr. Dalton his knowledge of, and taste for chemical and mathematical science. At Edinburgh, where he spent a year, he became a favourite pupil of Professor Leslie, and subsequently at the London University he gained in the year 1830, the highest prize in Natural Philosophy. His original destination was for calico-printing, which he pursued for a few years,

and for which his scientific acquirements eminently qualified him. During this period he published in the Philosophical Magazine for 1834, a paper entitled "Observations on Mr. Graham's Law of the Diffusion of Gases," which was republished *in extenso* in the Annales de Chimie et Physique, and attracted notice. This was followed by two short papers in Vol. XXV. of the same journal, on the same subject, and in Vol. XXVII. by a few additional observations.

Mr. Thompson died at Highgate after a short illness on the 14th of March, 1847, at the age of 36.

Since the last Annual Report the Society has published the 21st, 22nd, and 23rd parts of their Memoirs and Proceedings, the last part, completing the third published volume of our Transactions. These parts comprise the following communications :

1. "On the transformations produced by Catalytic bodies;" by Dr. Playfair.
2. "An analysis of the Ashes of the Orange Tree;" by Messrs. Rowney and How.
3. "On the Decomposition of Valerianic acid by the Voltaic current;" by Dr. Kolbe.
4. "On some experiments with Voltaic Couples;" by Mr. Adie.
5. "Upon the Chemical Constitution of Metacetonic acid, and some other bodies related to it;" by Messrs. Frankland and Kolbe.
6. "On the analysis of the Hop ash;" by Mr. Watts.
7. "On the Hydrates of Nitric Acid;" by Mr. A. Smith.
8. "On the products of the decomposition of Cuminate of Ammonia by heat;" by Mr. Fred. Field.
9. "Contributions to the Chemical history of Gun Cotton and Xyloidine;" by Mr. Gladstone.
10. "On the action of Nitric Acid on Cymol;" by Mr. Noad.
11. "On some of the products of Oxidation of Cumol by Nitric Acid;" by Mr. Abel.
12. "On the preparation of absolute Alcohol and the composition of proof spirit;" by Mr. Drinkwater.
13. "On Cochineal;" by Mr. de la Rue.
14. "On the Nitrates of Bismuth and Copper;" by Mr. Gladstone.
15. "On Crystallography;" by Dr. Leeson.

The Council has much pleasure in referring the Members, to the preceding list of communications, in proof not only of the activity and diligence, but of the skill and perseverance of their contributors; it is also gratifying to observe that many of those have had their origin in the laboratories of University College and of the College of Chemistry, under the sanction, advice and superintendence of the heads and directors of those and other public establishments.

At the last Anniversary Meeting, your Council was requested to consider whether any and what means could be devised for the purpose of

ensuring a more regular and efficient publication of the Society's Memoirs, and it has accordingly been determined, in order to promote the more speedy and regular circulation of the communications made to the Society, amongst its Members, to publish the Memoirs and Proceedings, which up to this time have appeared at irregular and indefinite intervals, in the form of a *Quarterly Journal*, one number of which it is intended shall appear on the 1st day of January, April, July and October in each year. And in order to render this *Quarterly Journal of the Chemical Society of London* more useful to the Members and acceptable to the public, it has been further resolved, that Notices of all important papers upon chemical subjects which may appear in foreign journals, shall be appended to each number of this Quarterly Journal; and further, that the January number of each year shall contain an alphabetical list of the heads of all Chemical papers which have appeared during the year, both at home and abroad, up to the time of publication of the Journal.

The attention of contributors to the Society's Memoirs is requested to the following resolution of the Council, dated April 13, 1841.

"The Society will not guarantee the printing of communications that shall have appeared in any periodical, Foreign or English, prior to their publication in the Transactions of the Society."

PRESENTS RECEIVED SINCE THE LAST ANNIVERSARY.

Journal of the Franklin Institute.

Silliman's American Journal.

The Journal of the Pharmaceutical Society of London.

Chemical Gazette to the 1st of January, 1848.

The Transactions of the Society of Natural History of Vienna.

The Proceedings of the Society of Natural History of Vienna.

The Journal of the Royal Agricultural Society of London, from the Author.

"A Treatise on Volcanoes;" by Dr. Daubeny, from the Author.

Miscellaneous Essays and Pamphlets, by Dr. Hare, Mr. Silliman, Professor Dana, Messrs. Ogsden and Way, and by Dr. Schunk, from the respective Authors.

Specimens of artificially crystallized oxide of zinc, from Mr. Herapath.

The following is the audited Report of the Treasurer for the year 1847.

AUDITED REPORT OF THE TREASURER.

Dr. ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON.

Cr.

		£.	s.	d.	£.	s.	d.
1847.	To Balance from last Account	377	2	3	1847.		
March 23.	To Half-year's dividend on £400, 3 4 <i>p</i> cent. off Income Tax	5	16	6	June 8.		
July 16.	"	"	"	"			
					By purchase of £400 3 4 <i>p</i> cent. Consols (@ 88 <i>f</i> £353, brokerage 10 <i>b</i> .) standing in the name of Robert Porrett, as Treasurer of the Chemical Society of London	353	10 0
1848.	To ditto	5	16	6	By Poundage and Postages to Collector	8	1 11
Jan. 15.	To Profit on sale of "Chemical Memoirs," published by R. & I. E. Taylor	6	7	4	By Rent paid to Society of Arts	25	0 0
March 27.	To Amount of Subscriptions received to this day	188	0	0	By Payment to A. Simmons for Tea and Coffee to 21st inst.	10	17 8
" 29.	"	"	"	"	By Ditto to Servants and Door-keeper of Society of Arts for 1 <i>½</i> years	2	5 0
					March 27. By Ditto for Book-binding	6	10 1
					" " By Ditto to D. Nutt for Chemical Periodicals	4	6 0
					" " By Ditto to H. Baillière for Books	5	9 6
					" " By Ditto to R. & I. E. Taylor for Printing	92	2 2
					" " By Ditto to Ditto for Philosophical Magazine and Memoirs	2	1 0
					" " By Ditto for a Minute Book, Stationery, &c.	3	3 0
					" 29. By Balance in the hands of the Treasurer	69	16 3
					£ 583 2 7		
					£ 583 2 7		

London, March 29, 1848.

R. PORRETT, Treasurer.

We have examined the above Account and find it correct.

GEORGE DIXON LONGSTAFF, } Auditors.  
CHARLES DAVY.

April 3, 1848.

Thomas Graham, Esq., Vice-President, in the Chair.

The First Report on the Coals suited to the Steam Navy, by Sir Henry De la Beche and Dr. Lyon Playfair, was presented by the Authors.

Messrs. G. F. Clark and J. S. C. Heywood, were elected Members of the Society.

The first part of a paper by Mr. Nesbitt, on the detection of Phosphoric Acid and Fluorine in analysis, was read, and also the following communication :

*XIV.—Analysis of the Thames Water. By GEORGE FREDERICK CLARK, Esq.*

It can scarcely be doubted that the composition of the Thames water has been repeatedly the subject of chemical investigation ; it appears, nevertheless, that no detailed analysis of it has been published, although an accurate knowledge of its nature must be very desirable on account of the great variety of processes for which this water is daily employed in our metropolis. It is evident that a single analysis cannot possibly afford anything like a satisfactory idea of the composition of the water of a river like the Thames. For this purpose it is necessary to investigate it at different localities and at different periods ; in a word, a series of analyses must be performed. As one of this series, suggested by Dr. Hofmann to several of his pupils, I undertook the analysis of the water as it is found before it has been polluted by the London drains and sewers. The water was accordingly collected on the 16th of December, 1847, from the middle of the river, two hours after high-tide, in the neighbourhood of Twickenham, which is fourteen miles from London Bridge.

The temperature of the water was  $9^{\circ}.5$  Cent. or  $49^{\circ}.1$  Fahr.

The temperature of the air being  $13^{\circ}$  Cent. or  $55^{\circ}.4$  Fahr.

The specific gravity of the water was 1.0003.

A careful qualitative analysis pointed out the presence of potash, soda, lime, magnesia, iron, alumina, chlorine, sulphuric acid, silicic acid, and organic matter.

A trace of phosphoric acid was also observed. Bromine and iodine could not be detected in the water, even after considerable concentration. The quantitative analysis gave the following results.

*A. Determination of the total amount of fixed constituents :*

Amount of water employed.	Amount obtained.	Per centage.
I. 1182.582 grms.	.378 grm.	.0319639
II. 1000.208 "	.323 "	.0322932
<i>Mean</i>		<i>·03212855</i>

**B.** Determination of sulphuric acid :

Amount of water employed.	Amount of sulphate of barytes obtained.	Percentage of sulphuric acid.
I. 610.293 grms.	.350 grm.	.0024265
II. 581.275 ,,	.330 ,,	.0024294
		<i>Mean</i> .0024279

**C.** Determination of chlorine :

Amount of water employed.	Amount of chloride of silver obtained.	Per centage of chlorine.
I. 610.65 grms.	.039 grm.	.0015794
II. 580.35 ,,	.038 ,,	.0016192
		<i>Mean</i> .0015993

**D.** Determination of silicic acid :

Amount of water employed.	Amount of silicic acid obtained.	Per centage of silicic acid.
I. 1182.582 grms.	.0045 grm.	.0003805
II. 1000.208 ,,	.0040 ,,	.0003999
		<i>Mean</i> .0003902

**E.** Determination of lime and magnesia :

Amount of water employed.	Amount of carbonate of lime obtained.	Per centage of lime.
a. I. 1000.598 grms.	.2096 grm.	.0117305
II. 906.002 ,,	.1899 ,,	.0117377
		<i>Mean</i> .0117341

Determination of magnesia in the filtrate from the oxalate of lime:

Amount of water employed.	Amount of pyro-phosphate of magnesia obtained.	Per centage of magnesia.
b. I. 1000.598 grms.	.0195 grm.	.0007140
II. 906.002 ,,	.0175 ,,	.0007077
		<i>Mean</i> .0007108

**F.** Determination of the alkalies :

Amount of water employed.	Amount of mixed chlorides obtained.
a. I. 1000.000 grms.	.0305 grm.
II. 1184.304 ,,	.0390 ,,

## Determination of potash :

	Amount of water employed.	Amount of chloride of platinum and potassium obtained.	Per centage of potassa.
b.	I. 1000.000 grms.	.0265 grm.	.0005105
	II. 1184.304 ,,	.0320 ,,	.0005205
			<i>Mean</i> .0005155

## Determination of soda :

	Amount of water employed.	Amount of chloride of sodium obtained.	Per centage of soda.
c.	I. 1000.000 grms.	.0022407 grm.	.0011867
	II. 1184.304 ,,	.0024679 ,,	.0013071
			<i>Mean</i> .0012469

31963.6 grms. of the water were evaporated down to 574.475 grms. The precipitate which was formed and separated weighed 5.558 grms.

## Determination of organic matter in the filtrate :

	Amount of filtrate employed.	Amount of organic matter burnt off.	Per centage upon the whole amount of water.
I.	81.520 grms.	.148 grm.	.0032629
II.	129.839 ,,	.236 ,,	.0032668
			<i>Mean</i> .00326485

## Determination of organic matter in the precipitate :

	Amount of precipitate employed.	Amount of organic matter burnt off.	Per centage upon the whole amount of water.
I.	.0925 grm.	.0090 grm.	.0016918
II.	.1565 ,,	.0155 ,,	.0017221
			<i>Mean</i> .00170695

## Determination of carbonic acid :

At the time of collecting the water, a syphon capable of containing .557 cubic centimeters of distilled water was filled three times and discharged into a bottle containing chloride of calcium and ammonia ; the precipitate which was formed, weighed when dry 0.937 grm.

	Amount of precipitate employed.	Amount of carbonic acid evolved.	Amount calculated on the whole precipitate.
I.	.4175 grm.	.136 grm.	.3052263 grm.
II.	.4585 ,,	.155 ,,	.3167611 ,,
			<i>Mean</i> .3109937 ,,

Per centage in the water .01860565.

From the preceding experiments, the ingredients are found to exist in the following proportions :

	In 100 liters, Grammes.	In a gallon, Grains.
Sulphate of potash . . . . .	·9542	·66794
Sulphate of soda . . . . .	2·8573	2·00011
Sulphate of lime . . . . .	·6439	·45073
Chloride of calcium . . . . .	2·5003	1·75021
Carbonate of lime . . . . .	18·2278	12·75946
Carbonate of magnesia . . . . .	1·4673	1·02711
Silicic acid . . . . .	·3902	·27314
Phosphoric acid . . . . .	traces	traces
Alumina . . . . .	traces	traces
Carbonate of oxide of iron . . . . .	traces	traces
Soluble organic matter . . . . .	3·2648	2·28536
Insoluble organic matter . . . . .	1·7069	1·19483
	32·0127	22·40889

Direct determination of fixed constituents . . . . . 32·1285 22·48995

Having deducted from the per centage of carbonic acid that portion in combination with lime and magnesia, the per centage of free carbonic acid was found to be ·0098289, corresponding to 513·44 cubic centimeters in 100 liters, or 1·4233 cubic inches in an imperial gallon.

The iron and alumina were not separated, but both were determined in the state of sesquioxides.

The mean result of two experiments gave ·00001335 per cent of the mixed sesquioxides.

From the foregoing analysis, it appears that the principal ingredient in Thames water in the neighbourhood of London is carbonate of lime, held in solution by free carbonic acid, and which would therefore be deposited upon continued boiling.

I cannot conclude this paper without mentioning the attention and kindness of my friend, Dr. Hofmann, in affording me every facility for the prosecution of the above analysis.

April 17, 1848.

The President in the Chair.

The following communication was read :

XV.—*Researches on the Volatile Bases.* By A. W. HOFMANN, PH.D.  
Professor at the Royal College of Chemistry.

I.—ON THE ACTION OF CYANOGEN ON ANILINE, TOLUIDINE, AND CUMIDINE.

In a Memoir,\* published some years ago, I described a series of chlorinated and brominated compounds, which stand in very intimate relation to aniline, although only part of them originate directly from that base. Independently of any special view respecting the constitution of these substances, we may consider them as aniline, which has exchanged a certain amount of hydrogen, for an equivalent quantity of chlorine or bromine. At a later period, in conjunction with Dr. Muspratt I† succeeded in preparing nitraniline, a compound which is derived from aniline in a similar manner; namely, by the exchange of hydrogen for the elements of the hyponitric acid.

To complete these researches, the action of iodine and cyanogen upon aniline had still to be studied. An investigation of this kind appeared to be of some interest, more particularly as the imperfect knowledge we possess at present respecting the influence of these electro-negative radicals on organic bodies, seemed to indicate a marked difference between their action and the effects which chlorine and bromine, so analogous in every other respect, produce under the same circumstances. A careful study of the action of cyanogen in particular, seemed to promise valuable results. We are already acquainted with a series of most remarkable organic cyanogen compounds, as cyanide of benzoyl and the cyanides of the alcohol radicals, which of late have been investigated with such beautiful results; all these compounds, however, have been produced by double decomposition of organic chlorides or sulphates with metallic cyanides; none of them have been obtained by the direct action of cyanogen. We possess at present no compound, the hydrogen of which, in conformity with the theory of substitution, is replaced by cyanogen, as we imagine it to be replaceable by chlorine, bromine, or the elements of hyponitric acid.

The experiments, which I have described in the following pages,

\* Liebig's Annalen, vol. LIII. p. 1. Memoirs of the Chemical Society, Vol. II, p. 266.  
† Ibid. vol. LVIII. p. 201. Ibid. Vol. III. p. 111.

relate only to the action of *cyanogen* on aniline and some of the analogous volatile alkalies, as toluidine and cumidine. The novelty of this reaction, as well as the great variety of metamorphoses arising from the compound nature of cyanogen, attracted my attention in the first instance, the behaviour of these substances with iodine being still under examination.

*Action of cyanogen on aniline.*—Cyanogen gas is absorbed by aniline, with the evolution of heat. After the colourless liquid has been exposed to the current for a few minutes, it assumes a yellow tint, which gradually darkens, until at last becomes dark brown, and perfectly opaque. The odour of hydrocyanic acid, which was perceptible in the beginning of the process, is soon replaced by that of cyanogen. If the vessel containing the liquid is corked at this period, and left for twelve hours, the odour of cyanogen will have entirely disappeared; the liquid emits a powerful smell of prussic acid, and we find that a mass of crystals has been deposited. If instead of pure aniline, a cold alcoholic solution of this body is treated in the same manner, we observe exactly the same phenomena. The crystals deposited from the alcoholic solution are, however, purer and more perfect; the anhydrous base completely saturated with cyanogen gas solidifying to a dark mass, which it is difficult to purify.

Having ascertained the identity of the products resulting in both cases, I always preferred working with alcoholic solutions.

The crystals which have been deposited from the liquid, contain, especially if a great excess of cyanogen has been employed, a variety of substances, of which two are formed in considerable quantity. If the action of the cyanogen has only been continued until the liquid smells strongly of it, the crystals are found to consist principally of *one* compound, with a variable but always slight admixture of another body. The composition of the new compound leads to the provisional name of *cyaniline*, which I shall make use of in the following pages.

*Preparation of cyaniline.*—The crystals of this body when separated from the solution are deeply coloured by the dark red mother-liquor which adheres to them. By repeated washing with cold alcohol, in which cyaniline is nearly insoluble, this colour may be almost entirely removed. It is, however, more economical, with regard both to time and alcohol, to dissolve the crystals (after separating the mother-liquor and washing once or twice with alcohol) in dilute sulphuric acid, when according to the duration of the action of the cyanogen, more or less of a reddish crystalline powder will remain behind. The sulphuric acid solution has a yellow tint, which is

scarcely altered by treatment with animal charcoal. On the addition of caustic ammonia to this solution, a copious, slightly yellowish, flowery precipitate is thrown down, evincing at once the basic nature of the new product. After separating the sulphate of ammonia, the base is still not perfectly pure, the yellowish colour not belonging to it. To remove the latter, the precipitate is dried and dissolved in a large amount of boiling alcohol, from which, at a temperature only a few degrees below the boiling-point, cyaniline separates in splendid iridescent crystalline plates. Sometimes, even after this treatment, the crystals are slightly coloured; one or two more crystallizations, however, yield them perfectly colourless. In operations of this kind, I found Plantamour's ebullition funnel very useful.

*Composition of cyaniline.*—The analysis of cyaniline afforded some difficulties, this body being very refractory and difficult of combustion. The formation of a crystalline film in the chloride of calcium tube could only be avoided by employing very long combustion tubes. This is the reason why the results of the first analyses of this body exhibit greater discrepancies than usually occur with the derivatives of aniline. Both hydrogen and carbon were found somewhat too high; the former on account of the sublimate, the latter in consequence of the formation of small quantities of binoxide of nitrogen. The later combustions were performed in very long tubes, the mixture having been made in the tube with a copper screw, to avoid increased attraction of moisture, and a long layer of copper turnings preventing the formation of binoxide of nitrogen. For every combustion, the substance was prepared by a special operation; in some cases oxide of copper was used, in others chromate of lead.

I. 0·3938 grm. of cyaniline gave :

1·0219 " " carbonic acid and

0·2300 " " water.

II. 0·2873 " " cyaniline gave :

0·7495 " " carbonic acid and

0·1602 " " water.

III. 0·2608 " " cyaniline gave :

0·6700 " " carbonic acid and

0·1415 " " water.

IV. 0·3272 " " cyaniline gave :

0·8417 " " carbonic acid and

0·1860 " " water.

V. 0·2766 " " cyaniline gave :

0·7170 " " carbonic acid and

0·1560 " " water.

- VI. 0·3808 „ „ cyaniline gave :  
 0·9892 „ „ carbonic acid and  
 0·2119 „ „ water.

These experimental numbers lead to the following composition per cent :

	I.	II.	III.	IV.	V.	VI.
Carbon . .	70·77	71·14	70·06	70·15	70·69	70·84
Hydrogen . .	6·48	6·19	6·02	6·31	6·26	6·18

The amount of nitrogen, although known as the complement of the carbon and hydrogen, was, nevertheless also directly determined. An analysis according to Dumas' method (but without the assistance of the air-pump), gave, as usual, a slight excess. A second determination was made by burning the base with soda-lime. In this operation, cyaniline, like all other aniline compounds, yields a large quantity of aniline, even when burnt in the longest tubes. In consequence of this behaviour, it appeared at the first glance impossible to ascertain the amount of nitrogen by means of this method. On some reflection, however, these difficulties appeared surmountable, provided the platinum salt of aniline should prove quite as insoluble in a mixture of alcohol and ether as the corresponding ammonio-chloride. In both these platinum compounds the equivalents of nitrogen and platinum are in the same proportion. If it were possible therefore to obtain the *whole* amount of nitrogen of the substance in the form of an indefinite mixture of the two platinum salts, this mixture would only require to be ignited in order to calculate the nitrogen from the platinum residue, in the usual manner. On experiment, I found that the platinum salt of aniline is rather soluble in the usual mixture of alcohol and ether, but that it may be washed without loss with absolute ether, to which a few drops of alcohol have been added, in order to increase its solvent power for bichloride of platinum. A great number of analyses performed in this manner, have given perfectly satisfactory results.

- VII. 0·4625 grm. of cyaniline, burnt in a current of carbonic acid gave :

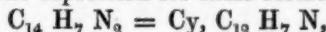
98 c. c. of moist nitrogen at 21° C. and 0·7593 Bar.

- VIII. 0·4485 grm. of cyaniline, burnt with soda-lime, gave :  
 0·7400 „ of platinum.

The per centage calculated from these numbers was :

	VII.	VIII.
Nitrogen . . .	24·15	23·40

The simplest atomic expression for these results is the formula :



as may be seen from the following table :

	Theory.			Mean of the experiments.
14 equivs. of Carbon . . . . .	84	<u>70·58</u>		70·60
7 , " of Hydrogen . . . . .	7	5·88		6·24
2 , " of Nitrogen . . . . .	28	23·54		23·77
	119	100·00		100·61

This formula is confirmed by the mode in which cyaniline is formed, by the decompositions which it undergoes, and by the analysis of several of its salts.

Three closely corresponding determinations by means of platinum, led to the equivalent 119·28; a gold determination gave 118·54, results coinciding with the theoretical number.

When I first discovered this body, I was inclined to regard it as a product of substitution analogous to chloraniline and bromaniline, a view which appeared to be supported by the simultaneous production of hydrocyanic acid.

The formula :



requires :

Carbon . . . . .	71·18
Hydrogen . . . . .	5·08
Nitrogen . . . . .	23·74
	100·00

It is at once obvious, that the amount of hydrogen corresponding with this formula cannot be reconciled with the quantity found. Moreover, an accurate investigation of the new base soon proved this view to be erroneous. Cyaniline is formed by the direct union of one equivalent of aniline and one equivalent of cyanogen; the production of hydrocyanic acid belonging to a totally different reaction.

*Properties of cyaniline.*—When repeatedly crystallized from alcohol, cyaniline appears in small, thin crystalline plates, which possess a peculiar silver-like lustre, and are perfectly colourless, tasteless, and inodorous. The slight solubility of the substance prevents the formation of large and well-formed crystals. Ether, pyroxylic spirit, bisulphide of carbon, benzol, fatty and ethereal oils are not better solvents of cyaniline than alcohol. It is perfectly insoluble in water.

The new base is not volatile without decomposition. At a tem-

perature of from  $210^{\circ}$  to  $220^{\circ}$  C. ( $442^{\circ}$  to  $450^{\circ}$  F.) it fuses to a yellow oil, which on cooling, solidifies with a crystalline structure. This fused mass is heavier than water, whilst the crystals float upon it. On heating the base a few degrees beyond its point of fusion, it is completely destroyed. The mass becomes brown, and is charred with the evolution of aniline and cyanide of ammonium, the vapours of which mechanically carry off a small quantity of extremely minute crystals of cyaniline, which escape decomposition. The base cannot be volatilized with the assistance of aqueous vapour. Its solutions are perfectly neutral.

Cyaniline no longer exhibits the reactions which are peculiar to aniline, and in some measure to the chlorine and bromine compounds. The solution of the base imparts no yellow colour to fir-wood; hypochlorite of lime, and dilute solutions of chromic acid, are likewise without action upon it.

*Compounds of cyaniline.*—The preparation of the salts of cyaniline is attended with some difficulty. The base, when dissolved in acids, soon undergoes a series of metamorphoses, its cyanogen being transposed with the elements of water in a peculiar manner, whilst aniline is reproduced. In order to avoid this decomposition, which I intend to describe to the Society in another paper, it is necessary to obtain the salts as fast as possible, in the solid form. This is the reason why those which are slightly soluble are most easily prepared.

The constitution of the salts of cyaniline is similar to that of the aniline salts. These compounds are, in fact, aniline salts, which have become associated with the elements of cyanogen. I have, however, vainly tried to obtain a salt of cyaniline by passing a current of cyanogen gas into an alcoholic solution of an aniline salt. Nitrate of aniline thus treated, undergoes no change, whilst a solution of the hydrochlorate gives rise to the production of new compounds, which I shall describe at another opportunity.

*Hydrochlorate of cyaniline.*—The base is nearly insoluble in concentrated hydrochloric acid; it dissolves, however, readily in dilute acid, but it is impossible to obtain the hydrochlorate from this solution by concentration. The crystals which are deposited on evaporation are no longer a compound of cyaniline; they are usually a mixture of various products of decomposition, containing traces of cyaniline, if the solution has not been too dilute, and amongst which a substance invariably occurs possessing a most remarkable odour, and which is produced likewise so frequently during the various metamorphoses of aniline, that it can scarcely have escaped the notice of those who have worked with that base.

The hydrochlorate, however, may be easily prepared in the following manner. Cyaniline is dissolved in boiling, dilute, hydrochloric acid, the yellow solution is filtered and mixed, while still hot, with an equal volume of fuming hydrochloric acid, when the liquid again becomes colourless and deposits, after a few minutes, an abundant quantity of white crystals. When washed once or twice with hydrochloric acid, and then with ether, these crystals are the pure hydrochlorate of cyaniline. This salt is extremely soluble in water and alcohol; it can be recrystallized from these liquids, but with considerable loss. The aqueous solution is distinguished by its sweet taste. It is so completely thrown down by fuming hydrochloric acid, that the filtrate no longer yields a precipitate with potash. If the solution of this salt be mixed with an aqueous solution of aniline, cyaniline is at once set free, showing that the basic properties of aniline are weakened by their union with cyanogen. Hydrochlorate of cyaniline, when perfectly dry, may be preserved without change; in the presence of moisture, however, it undergoes a gradual decomposition, becoming insoluble in water, and being soon entirely converted into other products.

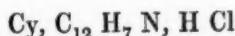
The analysis of this salt gave the following results :

- I. 0·3043 grm. of salt, burnt with chromate of lead, yielded :  
0·6028 " " carbonic acid and  
0·1495 " " water.
- II. 0·1398 " " of salt yielded :  
0·1274 " " chloride of silver.
- III. 0·3605 " " of salt of a second preparation yielded :  
0·3340 " " chloride of silver.
- IV. 0·3005 " " of salt of a third preparation yielded :  
0·2787 " " chloride of silver.
- V. 0·2687 " " salt yielded :  
0·2480 " " chloride of silver.

These numbers correspond with the following per centage composition :

	I.	II.	III.	IV.	V.
Carbon . .	54·02	—	—	—	—
Hydrogen . .	5·45	—	—	—	—
Chlorine . .	—	22·53	22·91	22·93	22·82

The formula :



requires the following numbers :

	Theory.	Mean of experiments.
14 equivs. of carbon	= 84·0	54·01
8 " " hydrogen	= 8·0	5·14
2 " " nitrogen	= 28·0	18·03
1 " " chlorine	= 35·5	22·82
1 eq. of hydrochlorate of cyaniline . . .	155·5	100·00

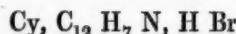
*Hydrobromate of cyaniline.*—All the statements which I have made respecting the preparation and the properties of the hydrochlorate, are equally true of the hydrobromate. On the addition of the concentrated acid, it crystallizes even with more facility than the hydrochlorate. A carbon determination and an estimation of bromine gave the following numbers :

- I. 0·3450 gm. of the salt, burnt with chromate of lead, gave :
  - 0·5355 " " carbonic acid and
  - 0·1260 " " water.
- II. 0·3448 " " the salt gave :
  - 0·3220 " " bromide of silver.

The composition per cent is therefore :

	I.	II.
Carbon . . . . .	42·33	—
Hydrogen . . . . .	4·05	—
Bromine . . . . .	—	39·25

The formula :



requires the following numbers :

	Theory.	Experimental numbers.
14 equivs. of carbon . . . . .	84·00	42·35
8 " " hydrogen . . . . .	8·00	4·03
2 " " nitrogen . . . . .	28·00	14·14
1 " " bromine . . . . .	78·26	39·47
1 eq. of hydrobromate of cyaniline	198·26	100·00

*Hydriodate of cyaniline.*—This salt closely resembles the two former, but is soon decomposed by the action of the atmosphere, iodine being separated.

Of the compounds of cyaniline with the so-called oxygen acids, I have obtained only the nitrate in a fit state for analysis ; this salt is difficultly soluble. Both the sulphate and oxalate are extremely

soluble. Their solutions when evaporated, are decomposed like the hydrochlorate.

*Nitrate of cyaniline.*—The base is easily soluble in boiling, dilute, nitric acid ; on cooling, a beautiful nitrate crystallizes in long white needles, which may be recrystallized, from boiling water, without decomposition. This salt is only slightly soluble in cold water, and even less so in alcohol and ether. It contains equal equivalents of cyaniline and of the hydrate of nitric acid. When burnt with oxide of copper, the following results were obtained :

I. 0·3244 grm. of the salt gave :

0·5504 „ „ carbonic acid and

0·1415 „ „ water.

II. 0·5292 „ „ the salt gave :

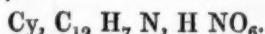
0·9019 „ „ carbonic acid and

0·2131 „ „ water.

Which numbers correspond to the per centage composition :

	I.	II.
Carbon . . . . .	46·27	46·48
Hydrogen . . . . .	4·80	4·47

leading to the formula :



as the following comparison with the theoretical numbers will show :

	Theory.	Mean of experiment.
14 equivs. of carbon . . . . .	84	46·15
8 „ „ hydrogen . . . . .	8	4·39
3 „ „ nitrogen . . . . .	42	23·07
6 „ „ oxygen . . . . .	48	26·39
1 equiv. of nitrate of cyaniline . . . . .	182	100·00

Nitrate of cyaniline forms a fine double salt with nitrate of silver.

*Platinum compound of cyaniline.*—A dilute solution of the hydrochlorate of cyaniline gives no precipitate with bichloride of platinum. On mixing, however, a boiling solution of the base in strong hydrochloric acid with a concentrated solution of bichloride of platinum, the double salt crystallizes on cooling, in beautiful orange-yellow needles, which become pure when washed with ether.

In the following determinations, different preparations of the salt were employed :

I. 0·3488 grm. of the platinum salt burnt with chromate of lead, gave :

0·3315 „ „ carbonic acid and

0·0758 „ „ water.

II. 0·3386 grm. of the platinum salt gave :

0·3220 " " carbonic acid and  
0·0790 " " water.

III. 0·4750 " " the salt being ignited, left :

0·1436 " " platinum.

IV. 0·1125 " " the salt left :

0·0340 " " platinum.

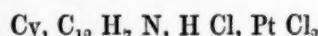
V. 0·1540 " " the salt left :

0·0470 " " platinum.

Per centage composition :

	I.	II.	III.	IV.	V.
Carbon . . .	25·93	25·93	—	—	—
Hydrogen . . .	2·41	2·59	—	—	—
Platinum . . .	—	—	30·23	30·22	30·51

The formula :



requires the following numbers :

	Theory.	Mean of experiment.
14 equivs. of carbon . . .	84·00	25·83
8 " " hydrogen . . .	8·00	2·46
2 " " nitrogen . . .	28·00	8·61
3 " " chlorine . . .	106·50	32·76
1 " " platinum . . .	98·68	30·34
1 equiv. of chloride of platinum and cyaniline . .	325·18	100·00

The solution of this double salt is decomposed with the same facility as the simple salts of cyaniline. It happened more than once that no crystals were deposited on cooling, too dilute a solution having been employed. On gently evaporating, the solution became turbid at a certain period, another salt in small crystals being separated which was found to be the platinum salt of aniline. On further concentration, brilliant octohedrons of the ammonio-chloride appeared. In most cases a mixture of both salts was obtained, with various products of decomposition. I once succeeded in hitting the point of concentration when only the aniline salt had formed. A specimen purified by washing with ether gave the following result :

0·2305 grm. of the platinum salt gave

0·0760 " or 32·97 per cent of platinum.

The aniline-platinum compound contains 32·98 per cent of platinum.

In several other determinations, numbers were obtained which indicated a mixture of aniline and ammonia.

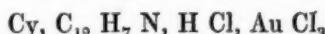
*Gold compound of cyaniline.*—This salt is obtained in the form of a yellow precipitate on adding a concentrated solution of terchloride of gold to an alcoholic or hydrochloric solution of cyaniline. In the latter case the solution should not contain too much free acid.

The analysis of a precipitate which had been washed with water and dried at 100° C gave the following result :

0·2423 grm. of the gold salt gave

0·1040 „ or 42·92 per cent of gold.

The formula



corresponds with the following values :

	Theory.	Experiment.
1 equiv. of hydrochlorate of		
cyaniline . . . . .	155·50	33·92
3 „ of chlorine . . . . .	106·50	23·21
1 „ of gold . . . . .	196·66	42·87
	<hr/>	<hr/>
1 „ of gold salt . . . . .	458·66	100·000

The gold salt of cyaniline is distinguished by its solubility in ether, a property belonging to various gold compounds with which I have lately become acquainted. The ethereal solution crystallizes on evaporation, but, in most cases the crystals are a mixture of the gold salts of cyaniline and aniline. The solution contains, besides, other products of decomposition. If the precipitate is dissolved in ether, when still moist, the salt is entirely decomposed, the crystals which are deposited consisting entirely of the pure aniline salt, which is no longer soluble in ether. The analysis of these crystals gave the following results :

0·2385 grm. of gold salt gave

0·1080 „ or 45·28 per cent.

The theoretical per centage of gold in the aniline-gold salt is 45·45.

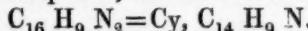
In the following table I subjoin the formulæ of the compounds analized :

Cyaniline . . . . .	Cy, $\text{C}_{12}\text{H}_7\text{N}.$
Hydrochlorate of cyaniline .	Cy, $\text{C}_{12}\text{H}_7\text{N, H Cl.}$
Hydrobromate of cyaniline .	Cy, $\text{C}_{12}\text{H}_7\text{N, H Br.}$
Nitrate of cyaniline . . . .	Cy, $\text{C}_{12}\text{H}_7\text{N, H NO}_6.$
Platinum salt . . . . .	Cy, $\text{C}_{12}\text{H}_7\text{N, H Cl, Pt Cl}_2.$
Gold salt . . . . .	Cy, $\text{C}_{12}\text{H}_7\text{N, H Cl, Au Cl}_3.$

I was curious to ascertain whether other bases were likewise capable of combining with cyanogen, in a manner similar to aniline. My attention was first directed to *ammonia*, which chemists are in the habit of considering as the type of the organic bases. I was quite unable however to obtain an ammonia compound analogous to cyaniline, although I brought the constituents into contact under various conditions; even in the anhydrous state.

*Toluidine* and *cumidine*, were naturally the objects of the next experiments, which, as might have been expected, were more successful.

*Cyanotoluidine*.—On treating an alcoholic solution of toluidine\* in the same manner with a current of cyanogen gas, the same phenomena take place which are observed with aniline. After a few hours, the red solution deposits a crystalline mass, from which the cyanotoluidine may be extracted with dilute hydrochloric acid. Potassa precipitates a white powder from this solution, which crystallizes from alcohol in small iridescent plates, in every respect resembling cyaniline. It is perhaps still less soluble in alcohol and ether than that base. I was satisfied with simply establishing the existence of this compound, which has evidently the composition:



*Cyanocumidine*.—The compound analogous to cyaniline is even more readily obtained from cumidine, the base which has recently been studied by Mr. Nicholson.†

An alcoholic solution of this body, when saturated with cyanogen, deposits after a short time long needles of the conjugate base. It is easily purified by repeated crystallization from boiling alcohol, in which it is far more soluble than cyaniline, so much so indeed, that the cold alcoholic solution is densely precipitated by water, whilst that of cyaniline is merely rendered turbid.

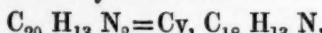
The analysis of this substance gave the following results:

0·1308 grm. of cyanocumidine gave

0·3565 „ „ carbonic acid and

0·0980 „ „ water.

These numbers lead exactly to the formula:



as may be seen from the following table:

\* The toluol which served for the preparation of toluidine had been obtained from light coal naphtha, in which, according to some recent investigations of Mr. Charles Mansfield, it is contained in considerable quantity.

† Quarterly Journal of the Chem. Soc. vol. 1. p. i.

	Theory.	Experiment.
20 equivs. of carbon . . .	120	74.53
18 " " hydrogen . . .	13	8.07
2 " " nitrogen . . .	28	17.40
1 eq. " cyanocumidine .	161	100.00
		100.00

I have also treated *nicotine* and *leucoline* with cyanogen gas. These two bases, however, although resembling aniline in a great many respects, seem nevertheless to belong to a perfectly different class of alkaloids. From nicotine and leucoline I vainly tried to produce the compounds corresponding to a large number of descendants which I derived by various processes from aniline, and whose analogues are easily obtained from toluidine and cumidine. Neither does cyanogen act on these latter bases as on aniline. The alcoholic solutions become brown, but neither crystals nor any basic product are deposited. I have not followed these changes quantitatively.

The formation of the bases described in the preceding pages offers one of the first instances in which an organic alkali is found associated with another compound, the presence of which does not affect its saturating capacity. The existence of such compounds might have been anticipated; there was no assignable reason why, among the bases, a mode of combination should be wanting, which in so many cases has been recognized among the acids. Since Professor Liebig\* first pointed out the constitution of formobenzoic acid, which both from its formation and decomposition he recognized as formic acid, associated with oil of bitter almonds—since that time up to the present moment, when in the hands of M. Dessaingues† we have seen hippuric acid splitting as it were into benzoic acid and glycicoll, so vast a number of analogous *conjugated organic acids* have been discovered, that this class of compounds may now be ranked amongst those which are best known.

*Conjugated organic bases* certainly exist in similar variety, and it is to be expected that the progress of science will soon add new members to the group we have just now become acquainted with. I may mention here that some researches on the action of chloride and bromide of cyanogen on aniline have elicited a new series of splendid alkaloids which evidently belong to the same class. In these substances which I intend shortly to describe to the Society, the basic atom of aniline is associated, not only with cyanogen, as in cyaniline, but

\* Liebig's Annalen, vol. x. p. 1.

† Idem, vol. LIX. p. 149.

with another very complicated compound in addition, the total weight of the adjunct considerably exceeding the equivalent of aniline.

The preceding investigation suggests a few remarks which I may offer here. Without entering at all upon the often-disputed question, whether the organic alkaloids are compounds of ammonia or amidogen, I cannot refrain from pointing out the influence which the formation of the new cyanogen bases is likely to exercise on some ideas which have of late been proposed, respecting the constitution of organic bases in general, the more so as those views seem to have emanated, partly at least, from my own researches.

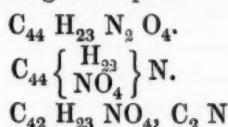
Our notions of a relation between the amount of nitrogen in organic bases and their saturating capacity emanating from Liebig's earlier experiments on this subject, lost their signification with the discovery of alkaloids containing more than one equivalent of nitrogen. Liebig's own subsequent researches, *i.e.* his investigations of melamine, ameline and amelide,\* left no doubt on this question; and since that period the class of similar bases has been considerably augmented. A relation between the nitrogen and the saturating capacity remained, nevertheless, extremely probable, and chemists now commenced to assume the nitrogen as existing in these bases under two different forms. In almost all cases, that portion of this element to which the basic properties were referred, was believed to be in the form of amidogen, ammonia, or oxide of ammonium, whilst the views respecting the other portion were for the most part less decided. Urea, *e. g.*, was considered by some chemists to be anomalous cyanate of oxide of ammonium, whilst it appeared to others as the ammonia compound of a nitrogenous oxide—oxide of urén.

*Nitraniline*, which I have described in conjunction with Dr. Muspratt, likewise contains two equivalents of nitrogen, and there can be no doubt in this case respecting the difference of form in which this element is present. Independently of any particular view respecting the nature of aniline, it is evident that half of the nitrogen in nitraniline is present in the state of an oxide, as nitrous acid or as hyponitric acid; whilst the other half belongs to the original atom of aniline. Now, based on the composition of nitraniline, Fresenius† has founded a general view of the constitution of the organic bases. According to his opinion, all alkaloids, the equivs. of which contain more than one equivalent of nitrogen are constituted similarly to nitraniline, they have to be considered as primitive bases, in which one or several equivalents of hydrogen are replaced by an equivalent amount of an oxide of nitrogen. The arbitrary nature of

\* Liebig's Annalen, vol. XVIII. p. 319.

† Idem, vol. LVIII. p. 322.

this view is obvious ;—what can entitle us to assume part of the nitrogen in an entire class of compounds as existing in this particular form, the occurrence of which, up to the present moment, has never been observed in vegetal productions. Among all the artificial bases, none are more dissimilar to the natural alkalies in most of their physical properties than the precise group to which nitraniline belongs. The preparation of cyaniline proves clearly that this additional nitrogen may exist just as well, and even with more probability, in the form of cyanogen. Fresenius considers strychnine, e. g., as an alkaloid containing hyponitric acid; with equal right, every other chemist might consider it as a cyanogen compound. Of the formulæ :



the first is certainly to be preferred, because it excludes every particular view of the constitution of this body, of which we are as yet entirely ignorant.

In a class of compounds so rich as that of the organic bases, a greater variety is certainly to be expected, than is admissible on the theory of my friend, Dr. Fresenius. Possibly some of the natural bases may contain an oxide of nitrogen, possibly others may be cyanogen compounds; however, a great many other modes of constitution may yet be imagined, which present a similar degree of probability. The form in which nitrogen is contained in an alkaloid can only be ascertained by a careful study of its products of decomposition. The existence of cyanogen in cyaniline is evident from the mode of its formation, but even had this base been first extracted from a plant, its decompositions, which in this paper I have scarcely mentioned, would have stamped it at once as a cyanogen compound.

A detailed investigation of the metamorphoses of the natural bases is greatly hindered by the costliness of the materials, but there is scarcely a field in organic chemistry the cultivation of which promises a richer harvest. The success which has attended the few experiments hitherto made in this direction, the production of leucoline from the bases of the quina bark, and the dissection of piperine into aniline and an organic acid, free from nitrogen, warrant the boldest expectations.

May 1, 1848.

The President in the Chair.

The following papers were read :

XVI.—*On some Phenomena of Capillary Attraction, observed with Chloroform, Bisulphuret of Carbon, and other liquids. By GEORGE WILSON, M.D., Lecturer on Chemistry, Edinburgh.*

THE phenomena of capillary attraction which appear, when one solid, and one liquid are brought together, have been extensively observed, and commented on by natural philosophers. Much less attention, however, appears to have been paid to what occurs when a single solid is in contact with two or more liquids of different densities, and which do not dissolve, or act chemically upon each other; although it cannot be doubted that an inquiry into this branch of the subject would bring to light novel facts, and might contribute greatly to the realization of a complete theory of capillary action.

I have happened, recently, to notice quite accidentally, some striking phenomena, which show themselves, when certain liquids denser than water, are exposed, while contained in glass or glazed porcelain vessels, to the alternate action of aqueous solutions of acids and alkalis. The object of this communication is to bring the phenomena observed before the Society as a slender contribution towards the extension of our knowledge of capillary attraction. I shall describe them at length, as manifested with chloroform, the liquid with which I have made most experiments, and afterwards refer briefly to the results obtained with other fluids.

When chloroform is placed in a test-tube, or other vessel of glass, standing on a horizontal surface, it exhibits, like other substances which wet that solid, a curved surface with the concavity upwards. If water or an aqueous solution of nitric, sulphuric, or muriatic acid, be poured over the stratum of chloroform, the surface of the latter immediately changes the direction of its curve, and becomes convex upwards; the convexity induced being much greater, however, than the previous concavity. If, on the other hand, an aqueous solution of potash, soda or ammonia be placed above the chloroform, the latter ceases at its upper limit to present a sensible curvature upwards or downwards, and shows a surface, which to the unassisted eye, appears to be flat. It is to this property of an acid to round, and of an alkali to flatten the surface of various liquids, of which chloroform is one, that I seek specially to direct attention.

The phenomena referred to, cannot seem remarkable when merely described; but they have appeared striking, and I may say, startling to most who have witnessed them. They are best observed by dropping into a perfectly clean, flat-bottomed glass vessel containing pure water, a quantity of chloroform too small in amount to touch the walls of the vessel on every side. The heavier liquid then shows itself, as a brilliant, highly mobile globule. If alkali be now added, the globule in a moment collapses, sinks as if exposed to a crushing force, and flattens out on the bottom of the glass. On slightly supersaturating the alkali with an acid, the flattened chloroform starts into its previous globular shape, with a momentum and rapidity, such as might be exhibited by a highly elastic substance, like a ball of caoutchouc suddenly relieved from enormous pressure. When the acid in its turn is supersaturated with alkali, the flattening again occurs, and by alternating the addition of these reagents, the same globule may be successively flattened and rounded for any number of times.

It is necessary here to mention, that the employment of an acid is not essential to the development of the phenomena described. In distilled water, chloroform exhibits a convexity of upper surface as marked as in the aqueous solution of an acid. The alternate addition to water, and removal from it of alkali, are as efficacious accordingly as the successive addition of alkali and acid. But the washing away of the former by repeated affusions and decantations of water, is a tedious and unsatisfactory process, which has the great disadvantage of changing the form of the globule by slow gradations from a flat to a convex surface, whilst an acid effects the conversion *per saltum*. I shall confine my observations, accordingly, to the action of alkalies and acids, although the effect of the latter in altering the shape of the chloroform globule, is not greater, but as I incline to think, less than that of water.

Change in configuration, however, is not the only alteration which the globule of chloroform undergoes. Some of its other physical properties are markedly altered by its contact with acids and alkalies. These changes are best seen when a deep white saucer, or flat-bottomed porcelain basin is made use of, as the containing vessel. When acidulated water is placed in this, and chloroform let fall into it, the denser fluid is scarcely wetted, and although nearly half as heavy again as pure water, sinks reluctantly.\* If the drops

\* The sp. gr. of chloroform is generally stated to be 1.480, but the density of pure specimens averages at least 1.494, according to the observation of my friend Mr. W. Swan.

indeed be small, they never reach the bottom, but floating on the surface, evaporate away. Those which descend, form globules very mobile, and readily obeying the solicitation of gravity. When separate globules meet, they rapidly flow together, and scarcely one is to be seen without a bubble of air attached to its upper surface, and adhering very tenaciously. I have already referred to the brilliancy of the drops of chloroform at the bottom of the water; they retain this character when the water is acidulated.

When the water, on the other hand is alkaline, the chloroform is quickly wetted, and sinks swiftly. The drops, if small, become circular discs with rounded edges; if large, they are oval, or spread out into elongated, irregularly ovoidal, or flattened cylindrical forms. Their shape, however, is changed by the slightest impulse, or inclination of the containing vessel, in a way which, perhaps, I may best illustrate by comparing it to the ever-varying elongations, contractions, and irregular swellings, which alter the configuration of an active living leech in a glass of water. The flattened globule, moreover, is much less mobile than the rounded one in acid. The former moves sluggishly, even down an inclination; clings to the vessel; and when compelled to move rapidly, leaves a tail behind it, like foul mercury. No air-bells attach themselves to it, and its brilliancy is sensibly diminished, as if its refractive index had altered.

The phenomena I have described are sufficiently striking when made with colourless chloroform; but I find that the addition of colouring matter to that liquid makes all of them much more conspicuous, and curiously modifies some of them. In reference to this subject, I premise, in case the fact has not already been put on record, that chloroform dissolves in whole, or in part, the colouring principles of turmeric and rhubarb root, of blue litmus, and of the false alkanet, (*Anchusa tinctoria*). It probably dissolves many other organic colouring matters, but those are the only ones I have tried. It can thus be made yellow, blue, and red, and although its solvent action on the substances referred to, is much inferior to that of water, alcohol and ether, chloroform becomes sufficiently deeply tinted to contrast strongly with colourless liquids. Its behaviour with these, is in consequence more readily observed, especially when capillary tubes are made use of. The litmus-blue chloroform keeps its colour worse than the turmeric or alkanet solutions, but it is preferable to them, for its tint is wholly unaffected by acids or alkalies, unless very concentrated; whilst these change the colour of red and yellow chloroform, and what is still more annoying to the experimenter, become coloured themselves.

When alkali is added to water in a porcelain vessel, at the bottom of which a globule of blue chloroform is lying, the latter flattens out much more than when not coloured; frequently spreading over an irregular area, five or six times greater than it occupied before the alkali was poured upon it. It is impossible to speak of its form, as no two coloured globules shape themselves alike. I can compare their appearance only to that of a thin, diffused cloud, which a casual observer would not readily believe was a dense liquid, identical with the brilliant globules which roll about under water, or an acid. The apparent viscosity of these extended globules is great, and their sluggishness and immobility much more striking than when uncoloured. The colouring matter appears here and there in dark specks, as if it had been abandoned by the chloroform, yet as soon as a sufficiency of acid is added, the diffused chloroform-nebula rapidly contracts, gathers as it were, all the colouring matter to itself, and springs up into an elastic-like globule, as deeply tinted, to appearance, as before the acid was added. In all probability, however, a little of the colouring matter is held only in suspension by the globule, for the water dissolves the chloroform without dissolving the litmus, and as the chloroform solution was originally saturated at its boiling point, it must, of necessity, part with some of the colouring matter.

Precisely similar phenomena are observed with the turmeric and alkanet solutions, only the chloroform and water alternately change their tint from yellow to brown, or from red to blue, as acid or alkali is added.

All the phenomena I have described, as observed with colourless chloroform, may likewise be seen with Dutch liquid ( $C_4 H_4 Cl_2$ ), a substance containing the same elements as chloroform, although in a different proportion, and scarcely distinguishable from it in odour. Bisulphuret of carbon also comports itself with acids and alkalies, as the liquids already mentioned do. Dutch liquid, however, is troublesome to prepare and purify, and sulphuret of carbon has an odour which many deem very offensive. Chloroform is the most pleasant of the three liquids to work with, and what is sold in the shops is pure enough for the purpose.

The volatile oils, which are heavier than water, likewise comport themselves under acids and alkalies like chloroform. Those which I have tried are, the oils of sassafras, of cloves, of cinnamon, and of bitter almonds, in their crude state. These oils, however, do not illustrate the phenomena so well as the three liquids mentioned before. The drops which do not sink, cannot evaporate away, so

that they soil the sides of the glass, and the alkali appears permanently to modify the oil.

Bromine also flattens under alkalies, and rounds under acids, when at the bottom of water; but the change is less perceptible than with the other liquids mentioned. The experiment, indeed, cannot be fully tried, owing to the rapid action of alkaline solutions on bromine, and the impossibility of exposing the latter to these, without chemical combination occurring.

These are all the liquids I have observed, which exhibit the phenomena described under the head of chloroform. They are, however, the only ones I have tried, so that I do not doubt many others will be found behaving towards acids and alkalies in the manner I have described.

I may here mention also, that besides the alkalies, lime-water and baryta-water flatten chloroform; likewise aqueous solutions of the carbonates of potash and soda, but not, so far as one trial can decide, the commercial carbonate of ammonia. Solutions of neutral and acid salts, so far as I have tried them, appear all to round the surface of chloroform. The solvent action of that substance, however, greatly limits the trial of experiments. All the liquids lighter than chloroform, except aqueous solutions, which I have tried, have been dissolved by it. The volatile oils, olive, castor, and cod-liver oil, ether, alcohol, bisulphuret of carbon, and wood-spirit, appear miscible in all proportions with it.

In conclusion, I would refer for a moment to a question connected with the theory of the phenomena recorded. In speculating on the causes of the phenomena of capillary attraction presented by a single liquid and a solid, there are at most but two *loci* of force to consider, the solid and the liquid. In seeking to explain the phenomena I have described, however, there are three possible *loci* of force, the two liquids and the solid, so that the problem becomes more complex.

I have looked anxiously for any appearance which might indicate whether alkalies ex. gr. in flattening chloroform, do so by direct action on that liquid, or on the solid constituting the containing vessel, or on both. I have not been able to find an *instantia crucis* as to this question; but without seeking to affirm that the alkali may not *immediately* modify the forces resident in the walls of the vessel, I think evidence can be adduced to show that the alkali does directly affect the mutual attraction of the particles of the chloroform and other liquids alluded to. I would refer, in proof of this, to three

facts : 1. Chloroform rapidly wets and sinks in alkaline solutions. 2. When chloroform is shaken with these liquids, it breaks into more numerous and smaller globules than in water or acids. The same phenomenon is still more observable with sulphuret of carbon, and with oil of sassafras, and of cinnamon, whose densities approach more nearly to that of water than that of chloroform does, so that their globules can be longer retained in semi-suspension in water, away from the solid, than in the case with chloroform. 3. When from a narrow pipette, an alkaline solution is dropped on a large globule of chloroform, under water, in a wide vessel, the globule begins to flatten before the alkali can have reached the bottom so as to act on the solid.

A consideration of these facts has led me, from the first, to think it probable that the action of the chloroform and the alkaline-water on each other, is more concerned in the production of the capillary phenomena described in the foregoing paper, than the influence of either or both liquids on the containing vessel. I offer this as an opinion, for I cannot demonstrate its truth experimentally; but apart from other reasons for holding it, I have been led to connect the flattening of chloroform under alkalies with the chemical affinity of the latter for it, and its rounding under acids with the comparative indifference which even the strong acids exhibit towards it. Chemical *affinity* may often justly be regarded as *attraction*, in the strictly physical sense of the term. The molecules of bodies, in many cases, come nearer each other when they combine chemically. This may be the case when chloroform and potash are converted by their mutual action into chloride of potassium and formic acid. The alkaline solutions made use of, in the experiments recorded, were in every case too weak to decompose chloroform; but this does not forbid the idea of the liquids coming into closer physical contact than they otherwise would have done, in virtue of a chemical affinity, which nevertheless does not rise high enough to effect combination or decomposition. A weak electrical current will polarize water and effect a temporary change in the molecular arrangement of its elements, although it may be too feeble to decompose the liquid. A similar power, *mutatis mutandis*, may be ascribed to weak alkaline solutions in their effect on chloroform; and the rounding effect of acids may be regarded as in great part negative, and so far limited to the removal of the alkali.

I refer to this attractive power of chemical affinity, only as a possible cause of the phenomena recorded, and as one cause at work

where more forces than one are probably concerned in producing the effect.\*

\* Mr. William Swan, who has been kind enough to make some observations, at my request, on certain of the physical properties of chloroform, which add to the facts I have put on record, has taken up the question in its purely physical or physico-mathematical relation, and formed a theory on the subject. The discussion is of too purely physical a character to have come within the sphere of the Chemical Society, otherwise Mr. Swan's paper would have accompanied or followed my communication. His essay will appear in the July number of the London and Edinburgh Philosophical Magazine. I direct the attention of those who are interested in the question discussed in the present communication, to that gentleman's paper, as containing many new facts and interesting speculations.

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## NOTICES

OF

### PAPERS CONTAINED IN THE FOREIGN JOURNALS.

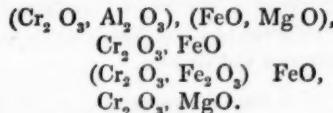
*On a new method of obtaining crystalline substances in the "dry way," and on the application of this method to the production of artificial minerals.\*—* M. Ebelmen has succeeded in crystallizing several artificial minerals by employing the solvent power of boracic acid, at a high temperature for the metallic oxides of which they are composed. The following is the plan pursued. Having weighed separately the substances that are to enter into the compound, and the fused boracic acid reduced to the state of powder, these are mixed with great care, and the powder is placed upon a leaf of platinum in a shallow cup of biscuit porcelain with a flat bottom. This cup is placed in a vessel composed of refractory clay, such as is used in baking porcelain. These vessels are cut slanting on one side, so as to establish an easy communication between the atmosphere of the furnace and the interior of the case, the volatilization of the boracic acid being thus facilitated by a constant current of air. They are then exposed to the heat of the porcelain furnace at Sèvres, during the entire period of firing.

As an example, the proportions used for preparing the rose-tinted spinelle ( $MgO$ ,  $Al_2O_3$ ) may be given, these were :

Alumina . . . . .	6.00	grms.
Magnesia . . . . .	3.00	"
Fused boracic acid . .	6.00	"
Green oxide of chromium	0.10 to 0.15	"

The mass, after being fired, is generally in the form of a rose-coloured cake, on the surface of which it is easy to distinguish the facets of equilateral triangles, but on detaching the product from the platinum, the interior is generally found to contain nests of rose-coloured crystals, which are very brilliant, and the form of which can easily be distinguished with a magnifier. The crystals are regular octahedrons truncated on the twelve edges ; they scratch quartz with ease.

Besides other varieties of spinelle, M. Ebelmen has produced cymophane ( $Al_2O_3$ ,  $GlO$ ), magnesian spinelle, aluminates of manganese, iron, cobalt, lime, and barytes, chrome iron and combinations of iron, magnesia and manganese, with oxide of chromium, corresponding to the formulae :



\* Ann. de Chim. et de Phys., xxii., 211.

Another series of experiments, not yet completed, proves that several silicates, which are infusible at the temperature of our furnaces, may also be prepared by the aid of boracic acid; for instance, the emerald and peridotite.

By using borax, which is less volatile, instead of boracic acid, alumina itself has also been crystallized, the proportions employed for this purpose were four parts of borax and one part of alumina, with  $\frac{1}{16}$  of oxide of chromium; after firing the mixture, a mass was obtained containing small ruby crystals, visible with the magnifier, which scratched the topaz and exhibited a crystalline form, that left no doubt as to the identity of the substance with corundum, the mineral next in hardness to the diamond. It is hoped, that processes of a similar nature to this will enrich chemical science with the knowledge of a series of new bodies, and that the facts elicited will enable geologists and mineralogists to form more precise notions with reference to the probable mode of production of natural minerals.

*On the errors which arise in the determination of the specific gravity of bodies, when they are weighed in a highly divided state.\**—In determining the specific gravity of gold, silver, and other solid bodies, Gustav Rose finds that the state in which the substance is weighed exerts considerable influence upon the result of the experiment.

Thus gold fused in a black-lead crucible, and pressed under a coining machine, had a specific gravity = 19.3365. Silver pressed in the same manner had a sp. gr. = 10.5665; whilst these two metals, in a state of minute division, possessed the following sp. gravities:

Gold precipitated by oxalic acid . . . . .	19.4791
Gold precipitated by protosulphate of iron . . . . .	20.6882
Silver precipitated from the nitrate by protosulphate of iron . . . . .	10.6139

Platinum, in the state of foil, has a specific gravity, varying between 21· and 22·; precipitated from the chloride by carbonate of soda and sugar, its specific gravity was found as high as 26.1418.

That this is not only the case with the metals, is shewn by experiments with sulphate of barytes. The specific gravity of pure varieties of the natural mineral varies between 4.4776 and 4.4875, whilst the precipitate from the chloride of barium by sulphuric acid, shews a specific gravity varying between 4.5209 and 4.5350.

Thus the determination of the specific gravity always affords a higher number, when the substance is weighed in the state of a fine powder, as procured by precipitation from solution, and the specific gravity is raised with the degree of fineness of the powder.

\* Pogg. Ann. LXXIII. p. 1.

The cause of this increase is explained, upon the assumption that the substances in the high state of division possess the property of condensing water, in the same manner as porous bodies condense gases. The body is, consequently, not weighed alone in water, but in conjunction with a film of condensed water. The loss experienced by the body in water is, therefore, diminished, and the product of this loss in the absolute weight of the body in air, or its specific gravity, is augmented in proportion.

Mechanical division has but little effect upon the specific gravity; it may, therefore, be practised, in order to avoid an error in an opposite direction, caused by cavities, &c. in natural crystals.

*On the fusion of Phosphorus.\**—The results of a very careful series of experiments instituted by M. Ed. Desains, are given as follows:—

- 1st. That the point of fusion of phosphorus is at  $44^{\circ}.2$  C.
- 2nd. That when a liquid is cooled below its fusing point, and then solidifies, its temperature does not always again attain the point of fusion.
- 3rd. That there is no sensible difference between the specific heat of liquid and solid phosphorus taken at the same temperature.
4. The specific heat of phosphorus is  $0^{\circ}.2$ , between 0 and 100 degrees C.
5. The latent heat of phosphorous is  $5^{\circ}.4$  C.

*On the double Salts of Pyrophosphoric Acid.\**—In the year 1834, Persoz noticed the tendency of pyrophosphoric acid to form double salts, and proposed the use of pyrophosphate of ammonia as a means of separating the oxide of nickel from oxide of cobalt. A process for gilding, invented by M. Roseleur, of Paris, in which pyrophosphoric acid is the solvent of the gold, and the rationale of which, as described by the author, appearing unsatisfactory, has induced M. Persoz to resume his researches upon some of the double salts of this acid.

When phosphate of soda or potash is added to a solution, in which a precipitate is formed, the precipitate, with few exceptions, is insoluble in an excess of the precipitant. When, on the contrary, a solution of pyrophosphated alkali is added to a saline solution, a precipitate is likewise formed, which, however, dissolves with as much ease in an excess of the precipitant as alumina, glucina, or oxide of chromium, dissolve in an excess of caustic potash, or oxide of zinc, copper or silver in an excess of ammonia. The pyrophosphates, containing a powerful base as those of lime, barytes, and silver, redissolve with the least facility in an excess of alkaline pyrophosphate. Some saline solutions are not rendered turbid by an alkaline pyrophosphate, as those of the salts of tin, gold, &c., all of which contain a very weak base. To explain these phenomena, the salts must be viewed as

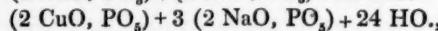
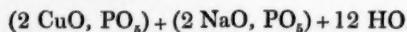
\* Ann. de Chim. et de Phy. xxii, 432.

† Ann. der Chem. und Pharm., lxv. p. 163.

bodies, which play the part of bases and acids towards each other, and are capable of entering into combinations of a higher order. If this view be admitted, it still remains to be demonstrated that the pyrophosphates of the alkalies really combine with other pyrophosphates, and form salts, in which the insoluble pyrophosphate plays the part of the electro-negative element, and the alkaline pyrophosphate that of the positive element. The first proof of the correctness of this view, may be derived from the extensive change, and sometimes total extinction, of the essential characters of the elements which have entered into the combinations. The characteristic taste of iron, and the peculiar colour communicated by its oxide, are entirely missed in the double compound of pyrophosphate of the peroxide of iron and soda, hydrosulphuric acid yields no precipitate of sulphur from this salt; and what is still more extraordinary, the salt is not precipitated, but rendered of a deep green colour, like that of manganate of potash, by hydrosulphate of ammonia.

The iron in this salt is, therefore, much more effectually retained in solution, and has undergone a greater change in its chemical properties, than in the combination into which it enters with tartaric and other fixed organic acids, and which are usually resorted to for the special purpose of preventing its precipitation. From these latter solutions, as is well-known, the iron is precipitated by an alkaline sulphuret. The iron is therefore, assumed to be differently located in these compounds than in the ordinary salts of iron. In an ordinary salt of iron, the acid *A* is the electro-negative element; the oxide of iron *B* is the electro-positive element. In a double salt, on the contrary, as in the pyrophosphate, *A B* becomes the electro-negative element, and *A' B'* the electro-positive; the polarity of the oxide of iron has thus been reversed.

Additional proof of the existence of the double pyrophosphates is obtained by the actual production of some of them in a crystalline form, and of constant composition. Thus two salts were obtained, containing copper and soda, the formulæ for which are—



from which the acid, when isolated, exhibited all the properties of pyrophosphoric acid.

Two methods are employed for the production of these salts. By the one method, a solution of alkaline pyrophosphate is added to the solution of the other salt until no further precipitate is produced; the insoluble pyrophosphate is then brought upon a filter, washed and digested with a solution of pyrophosphate of soda or potash, which acts the part of a base, and the solution is then submitted to spontaneous evaporation. There are two objections to this plan; the loss occasioned by washing the pyrophosphate, and the difficulty of obtaining solutions in a fit state for crystallization.

The second method consists in diluting a solution of the chloride or sulphate of the metallic oxide, which is to yield the insoluble pyrophos-

phate, so that too dense a precipitate is not formed; the alkaline pyrophosphate is then added, with constant agitation and great caution; any excess, beyond the quantity absolutely necessary for the solution of the precipitate, being avoided. The solution will then contain:

1. The double pyrophosphate.
2. The excess of alkaline pyrophosphate.
3. Sulphate of potash or soda, or chloride of potassium or sodium.

On the spontaneous evaporation of the soda compound, the excess of pyrophosphate of soda will crystallize first, then the chloride of sodium, or sulphate of soda, and, lastly, the double pyrophosphate.

If potash has been employed, chloride of potassium, or sulphate of potash, will be deposited first, then the double salt of pyrophosphoric acid, and the excess of pyrophosphate of potash will be found in the mother liquor.

The following salts were obtained, and are described by the author:

Pyrophosphates of magnesia and soda, of uranium and soda, of chromium and potash, of alumina and soda, of peroxide of iron and soda, of protoxide of iron and soda, of copper and soda, of copper and potash, of gold and soda. Besides these, combinations of the alkaline pyrophosphates, with pyrophosphates of the following bases:—oxide of bismuth, oxide of lead, oxide of cadmium, oxide of mercury, suboxide of mercury, suboxide of copper, oxide of nickel, oxide of cobalt, protoxide of tin, peroxide of tin, protoxide of palladium, peroxide of palladium, glucina, yttria, oxide of cerium, oxide of zinc.

Persoz considers it probable that pyrophosphoric acid may occur in nature (mineral waters?), and calls the attention of analysts to the necessity of taking means to determine the phosphoric acid always in the same form.

The presence of pyrophosphoric acid would nullify the results in the analysis of copper ores or alloys upon Pelouse's plan, although the presence of no other metal interferes with the process.

The beneficial results obtained by the use of iron in medicine, and particularly of those salts (tartrates), in which the presence of the iron is masked towards ordinary reagents, would appear to indicate a like or similar result from the use of the double pyrophosphates of that metal. In the case of the tartrate, the acid is consumed, or oxidized in passing through the system: this would not be the case with the double pyrophosphate.

The pyrophosphate of copper and potash, and those containing the oxides of tin, promise to be of service in calico printing.

*A new method of separating Magnesia from the Alkalies.*\*—Heintz separates the magnesia from solutions containing potash and soda in the following manner:—

The solution containing the three bases is supersaturated with ammonia,

\* Pogg. Ann., LXXIII. p. 119.

and if it contain no chlorides, a few drops of sal ammoniac are added. Should a troubled appearance arise in the liquid, it is treated with sal ammoniac until this vanishes. The magnesia is then precipitated by phosphate of ammonia, the precipitate washed with ammoniacal water, dried, heated to redness, and weighed. The free ammonia in the filtrate having been partly removed by boiling, the phosphoric acid is precipitated at the boiling temperature by nitrate or acetate of lead. When an excess of the lead salt has been used, a solution of carbonate of ammonia containing free ammonia is added to the hot liquid, which is then allowed to stand for some minutes. It is subsequently filtered, and the amount of potash and soda contained in the filtrate is ascertained by the usual methods.

It is essential that some chloride should be present in the solution, in order that one of the compounds of chloride and phosphate of lead (noticed at page 188) may be produced, from which ammonia cannot extract any phosphoric acid.

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*On the estimation of Magnesia by phosphate of soda, and that of Phosphoric Acid by magnesia.\**—The ordinary method of estimating the quantity of magnesia in solution, by means of tribasic phosphate of soda, is unobjectionable, when ammoniacal water is employed for washing the precipitate; but Weber has satisfactorily proved in the above Memoir, that phosphoric acid in the bibasic modification cannot be accurately determined by magnesia.

The phosphate of magnesia and ammonia, and the pyrophosphate of magnesia are not precipitated entirely by ammonia from solution in hydrochloric acid; neither is pyrophosphoric acid completely precipitated by the solution of a magnesian salt, even in the presence of ammonia, or an ammoniacal salt. Only, after standing for several weeks in the presence of ammonia, is the bibasic acid converted into the tribasic modification, and rendered capable of forming an entirely insoluble compound with magnesia.

If, therefore, the phosphoric acid in any substance is to be estimated by magnesia, it must first be ascertained by means of nitrate of silver, whether the acid exist in it in the tribasic or bibasic modification. If the latter is the case, the substance must be fused with from 4 to 6 parts of a mixture of equivalent quantities of carbonate of soda and potash, or treated for a length of time with concentrated sulphuric acid, by which means the bibasic acid and its compounds are converted into tribasic salts.

The pyrophosphates of lime, and the other alkaline earths, are, however, not entirely converted into tribasic phosphates by fusion with carbonated alkali; but by subsequent treatment with sulphuric acid and alcohol, the whole of the phosphoric acid may be obtained in the alcoholic solution.

\* Pogg. Ann. LXXIII. p. 137.

This must then be saturated with carbonate of soda, evaporated to dryness, and fused, in order to determine with accuracy the amount of phosphoric acid present.

*On the Separation of Nickel from Cobalt.\**—Liebig proposes the following plan for the quantitative separation of the oxide of nickel from oxide of cobalt. The mixture of the two oxides is warmed with hydrocyanic acid and potash (or pure cyanide of potassium), until complete solution is effected. The reddish yellow solution is then boiled to expel the free hydrocyanic acid; the compound containing protocyanide of cobalt is thus converted with the evolution of hydrogen into cobaltcyanide of potassium, and the nickel is contained in the solution as cyanide of nickel and potassium. When very finely divided oxide of mercury is added to the warm solution, the whole of the nickel is precipitated, partly in the state of oxide, and partly as proto-cyanide, and its place is taken by the mercury. The whole of the nickel and the excess of oxide of mercury are contained in this precipitate, which, when washed and heated to redness, leaves a residue of oxide of nickel entirely free from cobalt.

The liquid that has been treated with oxide of mercury, contains the whole of the cobalt as cobaltcyanide of potassium; in order to estimate the cobalt, it is supersaturated with acetic acid, and precipitated with a solution of sulphate of copper. This precipitation must take place at the boiling temperature, and the precipitate should be maintained at that heat for some time, or it will contain potash and remain slimy and difficult to wash.

The precipitate is cobaltcyanide of copper, it contains three equivs. of copper to two equivs. of cobalt; on treating it with potash, oxide of copper is precipitated, whilst cobaltcyanide of potassium remains in solution; the amount of cobalt may therefore be indirectly estimated by the amount of oxide of copper obtained.

If it is desirable to estimate the cobalt in a direct manner, the precipitate must be heated to redness, and the cyanogen destroyed; the residue is then dissolved in hydrochloric acid, with the addition of a few drops of nitric acid; a current of sulphuretted hydrogen gas is carried through the solution and the copper thus precipitated; from the filtrate, caustic potash will then precipitate oxide of cobalt, which must be well washed to remove every trace of potash, heated to redness and weighed. A portion of this may be reduced by hydrogen gas, and the entire amount of metallic cobalt calculated from the result.

The oxide of nickel, obtained by this process, does not afford a trace of cobalt when tested by the blowpipe.

The reduced cobalt must not be allowed to come into contact with the air as it is highly pyrophoric, although it loses this property when contaminated with the minutest quantity of nickel.

\* Ann. der Chem. und Pharm., LXV, 244.

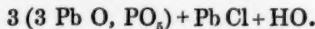
*On a new method of estimating Arsenic, Antimony, and Tin, in quantitative analyses.*\*—Sal ammoniac possesses the property of decomposing several metallic oxides at an elevated temperature, and of forming with the metals volatile chlorides. This property may be employed with advantage, according to H. Rose, in analysing compounds containing the acids of arsenic and antimony, or oxide of tin.

When an alkaline salt containing either of these metallic acids has to be analysed, after having been heated to redness and weighed, it is mixed, in the state of fine powder, with from five to eight times its weight of sal ammoniac, the mixture is placed in a small crucible of Berlin porcelain, covered with a concave lid of platinum, and heated until the whole of the chloride of ammonium is expelled. The alkali is left in the state of chloride, and can be weighed and estimated immediately. As long as chloride of ammonium is volatilized, there is no fear of loss in the alkaline chloride; when this ceases to be revolved, the heat is modified so as not to fuse the residue in the crucible. After having weighed the crucible, it is mixed with another portion of chloride of ammonium, and again heated to redness and re-weighed, in order to ascertain whether any further loss has been sustained. This operation must be repeated as long as the weight is diminished. The alkaline chlorides which remain are perfectly soluble in water, and there is not a trace of the metallic chlorides to be found mixed with them.

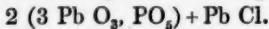
Professor Rose promises to show, in a future Memoir, a still more extensive application for chloride of ammonium in analytical chemistry.

*On the combinations of Oxide of Lead with ordinary Phosphoric Acid.*\*—Heintz has observed, when phosphate of lead is precipitated from a solution, containing at the same time a chloride, that the precipitate is always accompanied by chloride of lead, although it may have been washed until the water passes through without a trace of chlorine in solution. The precipitate formed under these circumstances is similarly constituted to the mineral *pyromorphite* ( $3(3\text{ Pb O, PO}_5) + \text{Pb Cl}$ ).

It may be obtained by adding a boiling solution of chloride of lead to a boiling solution of ordinary phosphate of soda, taking care that the latter be in excess, and is then found to consist of



A similar compound is obtained by reversing the previous operation, or by pouring the phosphate of soda into an excess of the chloride of lead; the precipitate which then falls is composed according to the formula,



The only method by which the author succeeded in obtaining a combination of 1 atom of phosphoric acid, with 2 atoms of oxide of lead, was by

\* Pogg. Ann. LXXIII, 582.

† Ibid. p. 122.

using a boiling solution of nitrate of lead, and precipitating with pure phosphoric acid. The precipitate is then white and crystalline, and is composed as represented by the formula,  $3 \text{ Pb O, PO}_5 + \text{HO}$ .

The salt containing 3 atoms of lead to 1 of acid ( $3 \text{ Pb O, PO}_5$ ) is best obtained by adding to a solution of acetate of lead an insufficient quantity of phosphate of soda, to precipitate the whole of the lead.

*On the Decomposition of Nitrate of Silver by heat.\**—In order to ascertain whether nitrate of silver was affected by a certain amount of heat, in the same manner as the alkaline nitrates, Persoz heated the salt in a small retort until gas bubbles were evolved from the melted mass, and red vapours began to appear. The gas which was collected before the appearance of the red vapours, proved to be pure oxygen, and the residue in the retort dissolved in boiling water, with the exception of a small quantity of pure metallic silver. The solution, when left to itself, deposited some very fine needles which were nitrite of silver, and the mother liquor contained the excess of undecomposed nitrate. On boiling this mother liquor for a short time with the silver that had been reduced in the previous experiment, in order to ascertain whether the nitrite had been formed by the action of the metallic silver on the nitrate (which does occur according to Proust), no similar salt was obtained. The whole of the nitrate could not be converted into nitrite by heat, for the nitrite alone was found more easy of decomposition than the nitrate, but it acquired stability by the presence of the nitrate of the same base, as also by that of an alkaline nitrate.

*Researches on the various platinum compounds derived from the green salt of Magnus.†*—These researches of M. Raewsky were undertaken

1st. With a view to determine whether a deposit of platinum always accompanied the formation of the platinum salt ( $\text{Pt Cl O, N}_2\text{H}_6, \text{NO}_5$ ) of M. Gros, in treating the green salt ( $\text{Pt Cl, NH}_3$ ) of Magnus with nitric acid, and whether the formation of that compound could not be explained by a chemical equation.

2nd. To confirm, by experiment, an idea thrown out by M. Laurent, that the radical of M. Gros was simply the radical of M. Reiset, in which the equivalent of hydrogen was replaced by chlorine; as in that case, by treating the radical of Reiset with bromine or chlorine, a substitution of hydrogen ought to take place.

3rd. To examine whether the white chlorinated compound of M. Peyronne yielded under the same circumstances, that is, on being submitted to the action of bromine or chlorine, the same products as those obtained

\* Ann. der Chem. und Pharm. LXXV. 178.

† Ann. de Chim. et de Phys., XXII, 278.

with the chlorinated radical of M. Reiset, and consequently to obtain additional proof of the identity of these two series of salts.

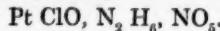
The results of the experiment were as follows :—

1st. The green salt of Magnus, notwithstanding the great variation in its physical properties, depending upon the mode of its preparation, is always constituted as represented by the formula :

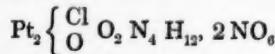


2nd. The formation of a grey deposit, presenting the appearance of platinum black, in the preparation of the salt of M. Gros, is an exceptional case, and must be referred to an incipient decomposition by heat of Magnus' green salt. This deposit does not appear to be pure platinum, as has been stated by M. Gros.

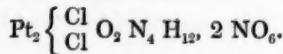
3rd. The action of nitric acid on the green salt of Magnus, presents two cases perfectly distinct. When an excess of acid is not used, the salt of M. Gros is obtained, corresponding to the formula :



If, on the contrary, an excess of acid is employed, instead of the salt of M. Gros, two other salts are obtained of very different composition, and belonging to two new series. One of these nitrates is insoluble, and is represented by the formula :

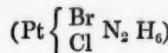


the other is soluble, and has the formula :



The elements are, therefore, grouped in the same manner in the two salts, and the only difference between them consists in an equiv. of chlorine in the second replacing an equiv. of oxygen in the first.

4th. The action of bromine on the binammoniacal protochloride of platinum of M. Reiset, and on that of M. Pyronne, is accompanied by no substitution; bromine combines with both these salts, in the same proportions, yielding the formula :



This result confirms what has been stated respecting the identity of these salts.

5th. The action of chlorine on the binammoniacal protochloride of M. Reiset, gives rise to two chlorinated compounds, the one of which represents the hydrochlorate of M. Gros, and the other, the same salt, plus one equiv of water. ( $\text{Pt Cl}_2, \text{N}_2\text{H}_6$ , and  $\text{Pt Cl}_2, \text{N}_2\text{H}_6, \text{HO}$ .)

*On the constitution of Taurin and of a body isomeric with it.\**—On making known the discovery of sulphur in taurin, Professor Redtenbacher observed that when taurin was treated with caustic potash and the residual mass moistened with dilute hydrochloric acid, sulphuretted hydrogen and sulphurous acid were evolved, as if pure sulphur had been treated with potash. The same process, conducted in a less violent manner, has at length thrown light upon the nature of this body.

When taurin is dissolved in a solution of caustic potash, and the solution is gradually evaporated to dryness, there occurs one period at which the whole of the nitrogen contained in the taurin is evolved as pure ammonia. If the evaporation is now stopped and the mass allowed to cool, the non-nitrogenized constituents of the taurin will be found as acids in combination with potash. Sulphuric acid now evolves sulphurous acid from the cold mass, without any deposition of sulphur or liberation of sulphuretted hydrogen, and when the fluid is distilled, acetic acid and some sulphurous acid is obtained in the distillate, whilst pure sulphate of potash remains in the retort.

Acetic acid, ammonia, and sulphurous acid are consequently the only products of this reaction; and taurin, according to Redtenbacher, is an acid sulphite of aldehyde ammonia, the elements of which are in a condensed state similar to those of cyanate of ammonia in urea.

If from taurine  $= C_2N\text{H}_7\text{O}_6\text{S}_2$  we deduct  
2 eqs. sulphurous acid =  $\text{O}_4\text{S}_2$ , the elements of  
aldehyde ammonia  $= C_4\text{N}\text{H}_7\text{O}_2 = C_4\text{H}_8\text{O} + \text{NH}_3 + \text{HO}$  remain;  
the ammonia was evolved during the process just described, and the aldehyde has been oxidized by the potash into acetic acid.

The author has succeeded in producing artificially the same compound of sulphurous acid with aldehyde ammonia, in which the elements are in a state of less intimate combination than in taurin. This body is obtained when sulphurous acid is carried into a solution of aldehyde ammonia in alcohol, and the product is cooled. The crystalline deposit is washed with alcohol upon a filter, and is then quite pure. It crystallizes in the form of prismatic needles, or in an irregular manner when the solution was allowed to become too hot. The crystals taste distinctly of sulphurous acid and aldehyde ammonia, and have an acid reaction. The dry salt is slowly decomposed by exposure to the air; at  $100^\circ\text{C}$ . ( $212^\circ\text{F}$ .) it becomes yellow and then brown, loses weight, and evolves an odour of burnt taurin. The following results were obtained from its analysis:

	By calculation.	By experiment.						Taurin.
		I.	II.	III.	IV.	V.	VI.	
4 eq. Carbon	300·0	19·2	19·08	49·41				19·28
1 " Nitrogen	175·0	11·2			11·98			11·25
7 " Hydrogen	87·5	5·6	5·66	5·97				5·73
6 " Oxygen	600·0	38·4						38·04
2 " Sulphur	400·0	25·6				25·79	25·30	25·24
1 " Acid =	1562·5	100-						25·70
= sulphite of aldehyde ammonia.								

\* Ann. de Chem. und Pharm. LXV, p. 37.

The formula for the salt is  $C_4N\text{H}_7\text{O}_6\text{S}_2$ , and it is consequently isomeric with taurin. The aldehyde must be contained in a condensed state in the salt, perhaps in the form of elaldehyde or metaldehyde. All the constituents are volatile, and yet the resultant compound is not so. Heated upon platinum wire over a spirit-lamp, it swells up, blackens, evolves an odour of burnt taurin, and leaves a residue of porous charcoal. It appears little altered when heated to  $100^\circ$  ( $212^\circ\text{ F.}$ ) in a tube closed at both ends, but becomes yellow at  $120^\circ$ — $140^\circ$  ( $248^\circ$ — $284^\circ\text{ F.}$ ), and a distinct smell of sulphurous acid is perceptible on opening the tube. The salt is difficultly re-obtained in crystals from an aqueous or an alcoholic solution, the greater portion being resolved into a gummy mass. The author only succeeded once, by very slow evaporation in a nearly close vessel, in recrystallizing the compound. Strong acids evolve sulphurous acid from the salt, and an ammonia salt of the acid is left. Potash exhibits the same reaction with it as with aldehyde. Salts of lead, barytes, and silver produce precipitates which are partially or totally soluble in acids. The silver salt is not blackened, and upon closer examination, contained mere traces of an organic body, and left more silver than would have been left by neutral sulphite of silver. The various means employed by the author for condensing the substance into taurin were unsuccessful.

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*Action of Nitric Acid on Brucine.\**—Rosengarten has repeated Laurent and Gerhardt's experiments on the action of nitric acid upon brucine, with somewhat different results. The French chemists affirm, that 1 equiv. of nitrous ether, 1 equiv. of cacotheleine= $(C_{42}\text{H}_{22}\text{N}_4\text{O}_{20})$ , and 2 equivs. of water, are the only products of the action of 3 equivs. of nitric acid upon 1 equiv. of brucine. Rosengarten treated fused brucine with cold nitric acid of 1·4 sp. gr., and obtained a gas, in which the carbon was to the hydrogen in one experiment as 4 : 6·05 equivs, and in another as 4 : 6·38 ditto. A relation, therefore, very different from that which exists in the varieties of ether. Two analyses of the residue, the so-called cacotheleine, the one portion crystallized from alcohol, and the other from water acidified with nitric acid, did not agree sufficiently close to enable the formula for this substance to be definitively fixed.

\* Ann. der Chem. et Pharm., LXV. p. 111.

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XVII. *On the Mineral Waters of Cheltenham.* By F. A. ABEL and THOS. H. ROWNEY, ESQRS., Assistants at the Royal College of Chemistry.

The unquestionably beneficial effects of mineral waters on various diseases of the human system, have attracted the attention of chemists from an early period to the composition of medicinal springs.

A great number of analyses of such waters have already been made, but our knowledge scarcely extends beyond that of the general effect produced by these medicinal productions; our speculations regarding the part taken by the individual constituents in the effects produced by mineral waters are very vague and divided. The unsatisfactory state of knowledge on this subject may be ascribed partly to the imperfect nature of most of the analyses, many of which were performed at a period when analytical chemistry was not so far developed as it now is, partly, likewise, to a want of principle and accordance in the arrangement of the results of many of these analytical investigations.

As long as these results are not arranged according to some one principle and rule, it is impossible for the medical man to institute a correct comparison between different waters, and much of the interest and use of such analyses is lost, as it is this comparison of different waters that is most likely to lead to a knowledge of the manner in which the individual constituents act.

A uniform and comparable arrangement of results, is of such primary importance, that the choice of the principle to be adopted is of less moment.

In the following analyses of different mineral waters from Cheltenham, suggested by Dr. Hofmann; the bases and acids have been arranged as much as possible according to their affinities, the strongest bases being supposed in combination with the strongest acids. Such an arrangement may be considered to furnish the nearest approach to the real distribution of the various constituents in the water.

With reference to the classification, this investigation may be regarded as the continuation of a work commenced by Messrs. Merck and Galloway on the analysis of the Bath waters, which is being carried out in the laboratory of the Royal College of Chemistry; where the analysis of a series of mineral waters, according to the system above described, is contemplated.

In order to collect the waters for analysis ourselves, we visited Cheltenham about the middle of August, 1847.

The springs of Cheltenham—of which there are at present fourteen in use—are distributed over the whole town and surrounding country. They are, however, conducted, by the various proprietors, through iron pipes to four different pump-rooms, which have been erected as near as possible to the principal wells. Having ascertained that many of the waters were very similar in properties and constitution, and as it would consequently have been a useless repetition to analyse the whole of them, we determined to select from among them, those that would best illustrate the entire series. As the waters of Montpelier Spa have been very recently analysed by Mr. J. T. Cooper, we selected such from the other spas as had never been investigated, or the analysis of which were of rather an ancient date. The waters chosen by us were the Cambray chalybeate spring, the two principal waters of the Royal Old Wells, and the so-called strong saline water of the Pittville Spa. We fixed upon the latter especially, on account of the discrepancies in the published analyses by Daniel, Daubeney and Buckmann.

The operations at the wells were the same as those generally performed; the only difficulty encountered, consisted in collecting the water for the determination of the gases contained therein. The wells being of great depth, and narrow in bore, it was impossible to descend, in order to dip the water by means of the usual siphon, nor could we lower a vessel, on account of the large cross-beams which traverse the inside of the wells; we were, therefore, compelled to content ourselves with filling the siphon from the force-pumps, and as these were

worked but slowly, drawing up the water from the bottom of the wells, we did not anticipate any very considerable loss of gases. In our paper on the "Artesian Wells of Trafalgar Square," we have shown by experiment, that the loss of carbonic acid, in the process of pumping up the water, is very trifling.

#### I.—CAMBRAY CHALYBEATE WATER.

This well was discovered in 1807, at Cambray, on the north side of the Chelt. (In 1803, a chalybeate water was discovered on the south side, which was subsequently closed up). It is situated under the kitchen floor of the proprietor's house; the water is conducted from thence, by means of iron pipes, over the little river Chelt to the pump-room, about 100 yards from the spring. The depth of the well is only about 7 feet. The temperature of the water at the time of observation was  $18^{\circ}$  C. ( $64,4^{\circ}$  F.) the temperature of the air being  $25^{\circ}$  C. ( $77^{\circ}$  F.) This water is liable to vary exceedingly in temperature, the well itself being under a house, and the pipe through which the water is conducted being near the surface, and in some places quite exposed. The reaction of the water is alkaline, it has a slight odour of hydrosulphuric acid, besides a very peculiar smell, similar to that of decomposing vegetable matter. Its taste is like that of all waters of this description. Its specific gravity we found to be 1,0010 at  $16,5^{\circ}$  C. ( $62,7^{\circ}$  F.) The water is perfectly clear when it issues from the pump, but becomes turbid almost immediately on standing, even in close vessels, depositing a quantity of sesquioxide of iron, with which all the vessels used in collecting the water are incrusted. By qualitative analysis, the water was found to contain a minute quantity of sulphuric acid, besides chlorine, carbonic, phosphoric and silicic acids, iron, lime, magnesia, potash, soda and organic matter. No bromine or iodine could be detected. A portion of the soda was found to exist as carbonate.

By quantitative analysis the following numbers were obtained :

#### A. Determination of the amount of fixed residue.

Water employed.	Amount of residue obtained.	Per centage in the water.
735,545 grms.	0,4759 grms.	0,0647

#### B. Determination of chlorine.

Water employed.	Silver-salt obtained.	Per centage of chlorine in the water.
I. 203,080 grms.	0,0364 grms.	0,00444
II. 232,942 ,,	0,0428 ,,	0,00454
<i>Mean</i>		0,00449
<i>o 2</i>		

*C.* Determination of silicic acid.

Water employed.	Silicic acid obtained.	Per centage in the water.
I. 616,402 grms.	0,0055 grms.	0,0009
II. 657,820 ,,	0,0072 ,,	0,00109
		<i>Mean</i> 0,00954

*D.* Determination of lime.

Water employed.	Carbonate of lime.	Per centage of lime in the water.
I. 616,402 grms.	0,2255 grms.	0,02049
II. 657,820 ,,	0,2420 ,,	0,02050
		<i>Mean</i> 0,020495

*E.* Determination of iron.

Water employed.	Sesquioxide of iron obtained.	Per centage of oxide of iron.
I. 616,402 grms.	0,0177 grms.	0,00258
II. 657,820 ,,	0,0168 ,,	0,002553
		<i>Mean</i> 0,0025665

*F.* Determination of magnesia.

Water employed.	Pyrophosphate of magnesia.	Per centage of magnesia.
I. 616,402 grms.	0,0534 grms.	0,00316
II. 657,820 ,,	0,0517 ,,	0,002879
		<i>Mean</i> 0,0030195

*G.* Determination of the alkalies.*a.* Estimation of the mixed chlorides.

Water employed.	Mixed chlorides obtained.	Per centage in the water.
I. 619,291 grms.	0,0999 grms.	0,01613
II. 578,692 ,,	0,0935 ,,	0,01615

*b.* Estimation of potassa.

Water employed.	Potassio-chloride of platinum.	Per centage of potassa.
I. 619,291 grms.	0,1550 grms.	0,00481
II. 578,692 ,,	0,1515 ,,	0,00502
		<i>Mean</i> 0,00492

For the determination of the small quantities of sulphuric and phosphoric acids, and the organic matter existing as apocrenic and crenic acids, and extractive matter, 40,04 lbs., or 18160,3422 grms. were evaporated to 405 grms. The precipitate obtained amounted to 9,4986 grms., and the filtrate, together with the washings, to 589,745 grms.

The sulphuric acid and extractive matter were determined in the filtrate (*a*), the phosphoric, crenic and apocrenic acids in the precipitate (*b*).

#### H. Determination of sulphuric acid.

Amount of filtrate ( <i>a</i> ) employed.	Sulphate of barytes obtained.	Per centage of sulphuric acid in the water.
I. 107,72 grms.	0,3047 grms.	0,000315
II. 96,800 ,,	0,2702 ,,	0,000313
<i>Mean</i> 0,000314		

#### I. Determination of phosphoric acid.

Amount of precipitate ( <i>b</i> ).	Pyrophosphate of magnesia obtained.	Per centage of phosphoric acid in the water.
1,4430 grms.	0,0167 grms.	0,000383

#### K. Determination of apocrenic acid.

Amount of precipitate ( <i>b</i> ).	Copper-salt obtained.	Per centage of apocrenic acid in the water.
1,4251 grms.	0,0100 grms.	0,00021

#### L. Determination of crenic acid.

Amount of precipitate ( <i>b</i> ).	Copper-salt obtained.	Per centage of crenic acid in the water.
1,4251 grms.	0,0359 grms.	0,0003467

#### M. Determination of carbonic acid.

533,533 cubic centimeters of the water yielded on treatment with chloride of calcium and ammonia in the usual manner, 1,6201 grms. precipitate, in which the carbonic acid was determined.

Amount of precipitate.	Carbonic acid.	Per centage in the precipitate.	Per centage in the water.
I. 0,5095 grms.	0,1750	34,3493 }	0,03466
II. 0,4717 ,,	0,1610	34,1320 }	

#### II.—PITVILLE SALINE WATER.

This water is procured from five wells, situated under the building or in the vicinity of the Spa. These wells empty themselves, by pipes,

into the main well, 90 feet in depth, which is situated under the pump-room. The temperature of the water was at the time of observation  $14^{\circ}$  C. ( $57.2^{\circ}$  F.) that of the air being  $19.5^{\circ}$  C. ( $67^{\circ}$  F.) Its reaction is strongly alkaline, it has a very slight odour of hydrosulphuric acid, and is possessed of a strong, but agreeably saline taste. Its specific gravity is 1,00763 at  $15.5^{\circ}$  C. ( $60^{\circ}$  F.) It was found to contain a large amount of sulphuric acid, an estimable quantity of bromine, and a distinct trace of iodine. The remaining constituents were the same as those found in the Cambray water, with the exception of iron, of which no trace could be detected. The phosphoric acid was not estimable.

*A. Determination of fixed residue in the water.*

Water employed.	Amount of residue obtained.	Per centage of residue.
153,335 grms.	1,4142 grms.	0.922294

*B. Determination of sulphuric acid.*

Water employed.	Sulphate of barytes obtained.	Per centage of sulphuric acid in the water.
I. 208,09 grms.	0,5624 grms.	0,09286
II. 273,206 „	0,7377 „	0,09277
<i>Mean</i>		0,092815

*C. Determination of chlorine and bromine.*

*a. Estimation of the precipitate by nitrate of silver.*

Water employed.	Amount of silver-salt.	Per centage of silver-salt.
I. 57,17 grms.	0,970 grms.	1,6966
II. 107,510 „	1,8235 „	1,6961
<i>Mean</i>		1,69635

*b. Estimation of the bromine.*

A known quantity of the mixed bromide and chloride of silver, perfectly dry, was submitted at a gentle heat, to a stream of dry and pure chlorine gas, the amount of loss, gave, by calculation, the amount of bromide of silver in the mixture.

Silver-salt employed.	Amount of loss.	Per centage of bromide of silver in the mixture.	Per centage of bromine in the water.
I. 1,1108 grms.	0,00137 grms.	0,008642	0,0036305
II. 0,7667 „	0,0009 „	0,008673	0,0036435
<i>Mean</i>		0,003637	

## c. Indirect estimation of chlorine.

Per centage of mixed silver-salt.	Per centage of chloride in the silver-salt.	Per centage of chlorine in the water.
1,69635	{ 1,687708 1,687677	0,417370 0,417362
		<hr/>
		Mean 0,417366

## D. Determination of silicic acid.

Water employed.	Amount of silicic acid.	Per centage in the water.
I. 388,61 grms.	0,0153 grms.	0,00394
II. 493,590 ,,	0,0197 ,,	0,00399
		<hr/>
		Mean 0,003965

## E. Determination of lime.

Water employed.	Amount of carbonate of lime.	Per centage of lime in the water.
I. 388,61 grms.	0,0427 grms.	0,006153
II. 493,590 ,,	0,0544 ,,	0,006172
		<hr/>
		Mean 0,006162

## F. Determination of magnesia.

Water employed.	Pyrophosphate of magnesia obtained.	Per centage of magnesia in the water.
I. 388,61 grms.	0,0836 grms.	0,007882
II. 493,590 ,,	0,1062 ,,	0,007883
		<hr/>
		Mean 0,0078825

## G. Determination of the alkalies.

## a. Estimation of the mixed chlorides.

Water employed.	Amount of mixed chlorides.	Per centage in the water.
I. 287,53 grms.	2,468 grms.	0,85834
II. 204,853 ,,	1,7585 ,,	0,8584

## b. Estimation of potash.

Water employed.	Amount of platinum double salt.	Per centage of potash in the water.
I. 287,53 grms.	0,0352 grms.	0,002356
II. 204,853 ,,	0,0235 ,,	0,00220
		<hr/>
		Mean 0,002278

54,16 lbs. = 24564,582 grms. of the water were evaporated to 574,58 grms.—8,193 grms. of precipitate (a) were obtained; the filtrate

(b), and washings amounted to 792,1670 grms. There being no apocrenic acid, nor any estimable quantity of phosphoric acid, the substances to be determined in the precipitate and filtrate, were crenic acid and extractive matter.

#### H. Determination of crenic acid.

Amount of precipitate (a) employed.	Copper-salt obtained.	Per centage of crenic acid in the water.
0,5515 grms.	0,0330 grms.	0,0005137

#### I. Determination of extractive matter.

Amount of filtrate (b) employed.	Amount of extractive matter.	Per centage in the water.
132,225 grms.	0,205 grms.	0,0049997

#### K. Determination of carbonic acid.

1611,20037 cubic centimeters of the water yielded with chloride of calcium and ammonia, 2,4540 grms. of precipitate, in which the carbonic acid was estimated.

Precipitate employed.	Amount of carbonic acid.	Per centage of carbonic acid in the precipitate.
I. 0,660 grms.	0,230 grms.	
II. 0,703 , ,	0,245 , ,	} 34,85
Per centage of carbonic acid in the water . .		0,05306

### III.—SULPHURETTED SALINE WATER. (NO. 1).

#### *Royal Old Wells.*

This, we were told, was the first water in Cheltenham discovered to possess medicinal properties. It was first noticed in 1716, that flocks of pigeons daily resorted to the head of a small stream in a meadow, distant a few furlongs south of the town, for the purpose of feeding on particles of a white salt casually formed from the water by the heat of the sun. The spring on its first discovery was found to be about 6 feet below the surface, in 1808 it was sunk and enlarged to the depth of 12 and width of 6 feet; and in 1819 it was further sunk to 72 feet, its present depth. It is situated close to the pump-room. The depth of water in the well at the time of observation was found to be 17 feet, the supply is said to be very regular. Its temperature was 14° C. (57,2° F.), that of the air being 22° C. (71,6° F.) It has a slightly alkaline reaction, and a pure saline taste. Although the odour of hydro-sulphuric acid was stronger in this than in the other waters examined by us, the

quantity present was not estimable. At 15.5° C. (60° F.) it has the specific gravity 1,0064. By qualitative analysis it was found to contain the same constituents as the Pitville water, besides iron existing as carbonate and phosphate. There are only small traces of potassa and iodine; part of the lime and magnesia exist as soluble salts, which are not precipitated by boiling. The following were the results obtained by quantitative analysis:

*A. Determination of the fixed residue.*

Water employed.	Amount of residue.	Per centage of residue in the water.
199,28 grms.	1,6291 grms.	0,817493

*B. Determination of sulphuric acid.*

Water employed.	Sulphate of barytes obtained.	Per centage of sulphuric acid in the water.
I. 67,13 grms.	0,3690 grms.	0,18887
II. 69,836 ,,	0,3822 ,,	0,18804
<i>Mean</i> 0,188455		

*C. Determination of chlorine and bromine.*

*a. Estimation of the mixed chloride and bromide of silver.*

Water employed.	Silver-salt obtained.	Per centage.
I. 47,52 grms.	0,5083 grms.	1,0696
II. 58,053 ,,	0,6210 ,,	1,0697
<i>Mean</i> 1,06965		

*b. Estimation of the bromine.*

Silver-salt employed.	Amount of loss.	Per centage of bromide of silver.	Per centage of bromine in the water.
I. 0,8554 grms.	0,0010	0,005447	0,002288
II. 1,2619 ,,	0,0015	0,005538	0,002326
<i>Mean</i> 0,002307			

*c. Indirect estimation of chlorine.*

Per centage of mixed silver-salt.	Per centage of chloride in the mixture.	Per centage of chlorine in the water.
1,06965	{ 1,064203 1,064112	0,263155 0,263177
<i>Mean</i> 0,263166		

**D.** Determination of silicic acid.

Water employed.	Silicic acid obtained.	Per centage in the water.
I. 421,16 grms.	0,0060 grms.	0,001425
II. 454,320 ,,	0,0067 ,,	0,001470
<i>Mean</i>		0,001447

**E.** Determination of perphosphate of iron.

Water employed.	Amount of perphosphate of iron.	Per centage in the water.
I. 421,16 grms.	0,0011 grms.	0,000261
II. 454,320 ,,	0,0012 ,,	0,000264
<i>Mean</i>		0,0002625

**F.** Determination of lime.*a.* Estimation of the total amount of lime.

Water employed.	Amount of carbonate of lime.	Per centage of lime in the water.
I. 421,16 grms.	0,1900 grms.	0,025263
II. 454,320 ,,	0,2047 ,,	0,02523
<i>Mean</i>		0,025246

A known quantity of water being submitted to brisk ebullition and the evaporated water replaced from time to time, a precipitate was formed; the iron, lime and magnesia were determined in the precipitate and filtrate in the usual manner.

*b.* Estimation of lime in the precipitate.

Water employed.	Amount of carbonate of lime.	Per centage of lime in the water as carbonate.
I. 432,72 grms.	0,1365 grms.	0,01766
II. 433,096 ,,	0,1367 ,,	0,01767
<i>Mean</i>		0,017665

*c.* Estimation of lime in the filtrate.

Water employed.	Amount of carbonate of lime.	Per centage of lime in the water as soluble salts.
I. 432,72 grms.	0,0583 grms.	0,007544
II. 409,73 ,,	0,0545 ,,	0,007448
<i>Mean</i>		0,007496

**G. Determination of iron.***a. Estimation in the original water.*

Water employed.	Amount of sesquioxide of iron.	Per centage of oxide of iron.
I. 421,16 grms.	0,0025 grms.	0,000534
II. 454,320 ,,	0,0027 ,,	0,000528
		0,000531

*b. Estimation in the precipitate formed on boiling.*

Water employed.	Amount of sesquioxide of iron.	Per centage of oxide of iron.
I. 432,72 grms.	0,0026 grms.	0,000540
II. 433,096 ,,	0,0025 ,,	0,000531
		Mean 0,000535

**H. Determination of magnesia.***a. Estimation of the total amount.*

Water employed.	Pyrophosphate of magnesia obtained.	Per centage of magnesia in the water.
I. 421,16 grms.	0,3868 grms.	0,033650
II. 454,320 ,,	0,4192 ,,	0,033807
		Mean 0,033728

*b. Estimation of magnesia in the precipitate formed on boiling.*

Water employed.	Pyrophosphate of magnesia.	Per centage of magnesia in the water as carbonate.
I. 432,72 grms.	0,016 grms.	0,001354
II. 409,73 ,,	0,0154 ,,	0,001377
		Mean 0,001365

*c. Estimation of magnesia in the filtrate.*

Water employed.	Pyrophosphate of magnesia.	Per centage of magnesia existing as soluble salts.
I. 432,72 grms.	0,380 grms.	0,032152
II. 433,096 ,,	0,3825 ,,	0,032359
		Mean 0,032455

**I. Determination of soda.**

Water employed.	Chloride of sodium obtained.	Per centage.	Per centage of soda in the water.
I. 21,41 grms.	0,129	0,6025	0,319481
II. 15,01 ,,	0,0896	0,5969	0,315789
			Mean 0,317638

84,286 lbs. = 38228,40116 grms. of the water were evaporated to 700 grms.—24,5965 grms. of precipitate (*a*), and 3295,7 grms. of filtrate (*b*), were obtained, in which the crenic acid and extractive matter were determined; apocrenic acid being absent, and phosphoric acid not estimable.

#### K. Determination of crenic acid.

Precipitate ( <i>a</i> ) employed.	Copper-salt obtained.	Per centage of crenic acid in the water.
1,2470 grms.	0,0180 grms.	0,024035

#### L. Determination of extractive matter.

Filtrate ( <i>b</i> ) employed.	Amount of extractive matter.	Per centage in the water.
50,1 grms.	0,016 grms.	0,000033

#### M. Determination of carbonic acid.

1609,2336 cubic centimeters of water yielded 2,2525 grms. of precipitate.

Amount of the precipitate employed.	Amount of carbonic acid.	Per centage in the precipitate.	Per centage in the water.
I. 0,6495 grms.	0,176 grms.	27,09	
II. 0,6215 „	0,168 „	27,03	
<i>Mean</i> 27,06			}

#### IV.—STRONG SALINE WATER. (No. 4.)

##### Royal Old Wells.

This well is situated at a short distance from the former. It is 71 feet deep, the height of the water at the time of examination being 12 feet; the supply at this spring is not so regular as at the former. Besides being conducted to the principal pump-room, the patients may partake of it in a small pump-room close to the well. It was here that the water was collected. Its temperature was 14° C. (57,2° F.), that of the air being 22° C. (71,6° F.). Its reaction is slightly alkaline, its taste saline, and it has a faint odour of hydro-sulphuric acid. Its specific gravity is 1,00795 at 15,5° C. (60° F.). Its constituents are similar to those of the former water. The iodine contained in it is estimable; of iron there are only traces, as also of phosphoric acid. The details of the quantitative analysis are as follows:

#### A. Determination of fixed residue in the water.

Water employed.	Amount of fixed residue.	Per centage in the water.
34,935 grms.	0,3702 grms.	1,059682

**B. Determination of sulphuric acid.**

Water employed.	Sulphate of barytes obtained.	Per centage of sulphuric acid in the water.
I. 42,27 grms.	0,0940 grms.	0,076408
II. 75,110 ,,	0,1672 ,,	0,076480
<i>Mean</i>		0,076444

**C. Determination of chlorine and bromine.***a. Estimation of the mixed silver-salt.*

Water employed.	Amount of silver-salt.	Per centage in the water.
I. 27,496 grms.	0,582 grms.	2,1166
II. 55,193 ,,	1,1660 ,,	2,1125
<i>Mean</i>		2,11455

*b. Estimation of bromine in the silver precipitate.*

Some of the mixed silver-salt was exposed, as before, to a stream of dry chlorine. From the amount of loss, the joint amount of bromide and iodide of silver in the precipitate was calculated.

Silver-salt employed.	Amount of loss.	Per centage of mixed bromide and iodide of silver.
I. 1,1813 grms.	0,0018 grms.	0,010143
II. 1,0761 ,,	0,0016 ,,	0,009895
<i>Mean</i>		0,010019

The per centage of iodide of silver is calculated from that of the iodine, obtained as described below, and deducted from the above per centage of mixed bromide and iodide of silver. The remaining 0,008968 per cent. of bromide of silver corresponds to 0,003767 per cent. of bromine in the water.

*c. Indirect estimation of chlorine.*

The per centage of bromide and iodide of silver being deducted from that of the mixed silver precipitate, leaves

2,104531 per cent. of chloride of silver, corresponding to 0,52045 per cent. of chlorine in the water.

**D. Determination of silicic acid.**

Water employed.	Amount of silicic acid.	Per centage in the water.
I. 326,105 grms.	0,0126 grms.	0,003864
II. 343,853 ,,	0,0137 ,,	0,003984
<i>Mean</i>		0,003924

**E.** Determination of lime.*a.* Estimation of the total amount.

Water employed.	Carbonate of lime obtained.	Per centage of lime in the water.
I. 326,105 grms.	0,0796 grms.	0,013669
II. 343,853 ,,	0,0837 ,,	0,013630
<i>Mean</i>		0,013649

*b.* Estimation of lime in the precipitate formed on boiling the water.

Water employed.	Carbonate of lime obtained.	Per centage of lime existing in the water as carbonate.
I. 469,95 grms.	0,0721 grms.	0,008591
II. 454,536 ,,	0,0697 ,,	0,008587
<i>Mean</i>		0,008589

*c.* Estimation of lime in the filtrate from the precipitate.

Water employed.	Carbonate of lime obtained.	Per centage of lime existing in the water as soluble salts.
I. 469,95 grms.	0,0410 grms.	0,004886
II. 454,536 ,,	0,0402 ,,	0,004950
<i>Mean</i>		0,004918

**F.** Determination of magnesia.*a.* Estimation of the total amount of magnesia.

Water employed.	Pyrophosphate of magnesia obtained.	Per centage of magnesia in the water.
I. 326,105 grms.	0,0960 grms.	0,010786
II. 343,853 ,,	0,1017 ,,	0,010836
<i>Mean</i>		0,010811

*b.* Estimation of magnesia in the precipitate formed on boiling.

Water employed.	Pyrophosphate of magnesia obtained.	Per centage of magnesia as carbonate.
I. 469,95 grms.	0,0266 grms.	0,002284
II. 454,536 ,,	0,0282 ,,	0,002273
<i>Mean</i>		0,002278

## c. Estimation of magnesia in the filtrate.

Water employed.	Pyrophosphate of magnesia obtained.	Per centage of magnesia existing as soluble salts.
I. 469,95 grms.	0,1085 grms.	0,00848
II. 454,536 ,,	0,1087 ,,	0,008359
		<i>Mean</i> 0,008419

## G. Determination of soda.

Water employed.	Chloride of sodium obtained.	Per centage.	Per centage of soda in the water.
I. 35,165 grms.	0,336 grms.	0,955495	0,505876
II. 21,466 ,,	0,2050 ,,	0,9549	0,505450
		<i>Mean</i> 0,955197	<i>Mean</i> 0,505663

50,3975 lbs. = 22858,07843 grms. of the water were evaporated to 941,5 grms. There were obtained, 7,727 grms. of precipitate, and 2242,8 grms. of filtrate, including the washings.

In the precipitate (*a*) the crenic acid was determined, in the filtrate (*b*), the iodine and extractive matter.

## H. Determination of iodine.

91,394 grms. of the filtrate (*b*) were evaporated to dryness with carbonate of soda, the residue was digested in strong alcohol, the solution thus obtained was again evaporated, and the residue once more heated with alcohol. On the evaporation of this alcoholic extract, a small residue was obtained, which was dissolved in water. On the addition of protochloride of palladium to the clear solution, it became turbid, and after standing for some hours, deposited a blackish precipitate of protiodide of palladium, which was collected on a weighed filter, first washed with water, then with alcohol, and finally, with a little ether. It was then dried at a low temperature, and the iodine calculated from the amount obtained.

Filtrate ( <i>b</i> ) employed.	Palladium salt obtained.	Per centage of iodine in the water.
91,394 grms.	0,0075 grms.	0,000567

## I. Determination of crenic acid.

Precipitate ( <i>a</i> ) employed.	Copper-salt obtained.	Per centage of crenic acid in the water.
1,0185 grms.	0,0555 grms.	0,000476

**K.** Determination of extractive matter.

Filtrate ( <i>b</i> ) employed.	Amount of extractive matter.	Per centage in the water.
68,67 grms.	0,1805 grms.	0,025790

**L.** Determination of carbonic acid.

1611,71205 cubic centimeters of water yielded 1,6615 grms. of precipitate.

Precipitate employed.	Carbonic acid obtained.	Per centage in the precipitate.	Per centage in the water.
I. 0,5435 grms.	0,173 grms.	31,83	
II. 0,6615 ,,	0,212 ,,	32,04	
		<hr/>	31,935

From the above analytical results the following composition of the four waters has been deduced:

## ON THE CHELTENHAM WATERS.

	I. Cambray chalybeate spring.		II. Pitville strong saline water.		III. Sulphuretted saline water, (No. 1.) Royal Old Wells.		IV. Strong saline water, (No. 4.) Royal Old Well.	
	Grms. in 100 kilogr. (liters).	Grains in an imperial gallon.	Grms. in 100 kilogr. (liters).	Grains in an imperial gallon.	Grms. in 100 kilogr. (liters).	Grains in an imperial gallon.	Grms. in 100 kilogr. (liters).	Grains in an imperial gallon.
Sulphate of potash	0.683	0.4781	4,216	2,9512	traces	traces	traces	traces
Chloride of potassium	7.213	5,0491	161,238	112,8666	..	..	135,630	94,9410
Sulphate of soda	1.734	1,2138	681,419	481,1933	334,666	234,0562	843,330	590,3310
Chloride of sodium	..	..	4,704	3,2928	..	..	..	..
Iodide of sodium	..	..	traces	traces	traces	..	..	..
Carbonate of soda	5.981	4,1867	28,783	20,1481	..	..	..	..
Chloride of magnesium	..	..	..	..	75,171	52,6197	11,429	8,0003
Bromide of magnesium	..	..	..	..	..	..	4,376	3,0632
Iodide of magnesium	..	..	..	..	..	..	0,623	0,4361
Carbonate of magnesium	6.232	4,3624	16,271	11,3897	..	..	9,2575	6,8026
Chloride of calcium	..	..	..	..	..	..	..	..
Bromide of calcium	..	..	..	..	..	..	..	..
Phosphate of lime	0.797	0.5579	traces	traces	..	..	..	..
Carbonate of lime	35,887	25,1209	11,003	7,7021	..	..	..	..
Perphosphate of sesquioxide of iron	..	..	..	..	..	..	..	..
Carbonate of iron	4.134	2,8938	..	..	..	..	..	..
Silicate acid	0.954	0.6678	3,965	2,7755	..	..	..	..
Apoacetic acid	0.210	0.1470	..	..	..	..	..	..
Crenic acid	0.347	0.2429	0.513	0.3591	..	..	..	..
Organic extractive matter	0.014	0,0098	4,999	3,4993	..	..	..	..
	64,186	44,9302	923,111	646,1777	814,921	570,4447	1059,669	741,7683
Fixed residue found by direct exper-	64,700	45,2900	922,294	645,6058	817,493	572,2451	1059,682	741,7774
iment	cubic centime.	cubic inches in	cubic centime.	cubic inches in	cubic centime.	cubic inches in	cubic centime.	cubic inches in
Amount of free carbonic acid at the	62,459	an imp. gallon.	58,634	an imp. gallon.	16,254	an imp. gallon.	in a liter.	an imp. gallon.
stated temperatures	traces	traces	traces	traces	traces	traces	traces	traces
Hydrosulphuric acid								

Before entering upon the comparison of our analyses with those previously made, we may mention, that on arranging the results obtained with the saline water, it was found, that the lime and a portion of the magnesia which was not precipitated by boiling the water, must exist as carbonates held in solution by the alkaline salts. It is well known that carbonate of lime is not absolutely insoluble in water (according to experiment, 1 part of carbonate of lime requires about 10,000 parts of water), and that this solubility is increased if carbonate of ammonia and caustic ammonia be present in the water, (1 part then requiring only about 6,800 parts of ammoniacal water). We have satisfied ourselves by direct experiment, that the solubility of carbonate of lime is much increased by the presence of chloride of sodium and sulphate of soda, at least, if we may judge from the precipitate which oxalate of ammonia produces in these solutions, the precipitate in water or ammoniacal water by the same reagent being scarcely perceptible. The slight solubility of carbonate of lime in water containing alkaline salts, makes it very desirable for the accurate determination of the alkalies, to add, after the addition of carbonate of ammonia, a few drops of oxalate of ammonia, to remove the last traces of lime, or of baryta, which have served for the separation of magnesia.

On glancing over the synoptical table, in which we have collected the results of the different analyses, we are at once struck by the small quantity of fixed constituents contained in the Cambray water, when compared with that of the other three; whilst the latter three contain between 500 and 800 grains in the imperial gallon, we find in the Cambray water not more than 64 grains, a quantity scarcely exceeding the amount of fixed constituents in common well-water. Again, we observe, quite irrelative of the amount of fixed substances, that they differ also very considerably with regard to their nature. The four waters possess an alkaline reaction, but whilst this reaction is most prominent in the Cambray and Pitville waters, which contain a considerable amount of carbonate of soda, the alkalinity of the other two is scarcely perceptible, and only becomes manifest on evaporation, arising evidently from the decomposition of the large quantity of chloride of magnesium which these waters contain. The Cambray and Pitville springs are therefore carbonated alkaline, while the others are carbonated saline, waters.

Our analyses of these waters differ very considerably from all others previously published. In all the four which we examined, potash was detected in larger or smaller quantities; of this no mention is made in any other analysis, excepting one by Seudamore, who

states, that potash exists in small quantity in one of the waters of the Royal Old Wells.

In a paper by Dr. Daubeney\* on the presence of iodine and bromine in the brine springs of England, it is stated that no bromine is found in those springs of Cheltenham which contain iodine, whilst in the Pittville spring, the only one not containing iodine, every six gallons contain about 1 grain of bromine. In three of the waters analysed by us, we found bromine in estimable quantities, accompanied always by small amounts of iodine.

The phosphoric acid has also been overlooked in these springs.

Respecting the gaseous constituents, the large quantity of carbonic acid is at once obvious, especially in the sulphuretted and saline water; it far exceeds the quantity contained in the King's Well at Bath.

Small quantities of hydrosulphuric acid were found in all the Cheltenham waters, but in none of those which we collected was it capable of being estimated. In the analyses of the old wells, published some years ago by Scudamore,† the amount of hydrosulphuric acid is stated to be not only estimable, but very considerable. Dr. Gairdner, in his work on thermal springs,‡ mentions, however, that the quantity of this gas in these waters varies exceedingly, being always much greater in rainy seasons.

The most probable view with respect to the formation of this gas seems to be the decomposition of the sulphates by the organic matter contained in the water. In support of this, we may mention that a stone bottle full of the water from Pittville, which scarcely contains a trace of hydrosulphuric acid, was found, on being opened shortly after its arrival in London, to be highly charged with this gas—which phenomenon could only arise from the presence of some particles of cork which had accidentally fallen into the water—as other quantities of the same water were kept for a great length of time in stoppered bottles without undergoing the slightest change.

Several views have been adopted to explain the formation of the mineral springs of Cheltenham. The most probable appears to be that of Sir R. Murchison, which is mentioned in his work on the Geology of Cheltenham. He supposes the springs to arise from the new red sand-stone, where they become impregnated with saline ingredients, and, passing up through crevices in the lias, and through

\* Philosophical Transactions, May, 1830.

† A chemical medical report of the properties of the mineral waters of Buxton, &c., by C. Scudamore, M.D. 1820.

‡ Thermal and mineral springs, by Dr. Gairdner, 1832.

various strata of marl and clay, loaded with iron pyrites, these ingredients undergo certain chemical changes, one of which he presumes to be the formation of sulphuric acid, which combines, in its passage upwards, with various bases. He hence concludes, that those springs which are of the greatest depth, having the largest amount of strata to pass through, acquire the most valuable properties.

It is a well known fact that the strength and constitution of the Cheltenham waters are very inconstant, and that frequently, springs which have hitherto been valuable, will suddenly be deprived of so large an amount of ingredients, that the proprietors are forced to abandon them. The supply at most of the springs is limited, as is shown by the fact, that numbers of wells are sunk, in order to supply one main well properly. The late Mr. Thompson, of Montpelier, went to a very great expense in sinking a large number of deep wells, in the surrounding country, at the distance of some miles from his Spa, in order that he might obtain a proper supply. Expensive precautions have likewise been taken by the various proprietors to prevent the waters becoming adulterated by rain-water that might penetrate through the upper soil into the wells, by making the higher portions of these perfectly impermeable to moisture. It must be admitted by the most sceptic, that these facts are wholly irreconcileable with the suppositions of many people, that the Cheltenham waters are artificially impregnated by the proprietors; a supposition that has most likely arisen from the circumstance, that there is a laboratory adjoining the Montpelier Spa, where the water is evaporated, in order to obtain the salts, as also from the knowledge, that so-called Cheltenham salts are prepared artificially in that town, and by chemists all over the country.

The following is a tabular view of all the published analyses of the Cheltenham waters we have been enabled to procure:

[SEE TABLE.]

In conclusion we cannot refrain from noticing the great readiness with which the proprietors of the various Spas furnished us with every opportunity and convenience for examining their wells and arrangements.

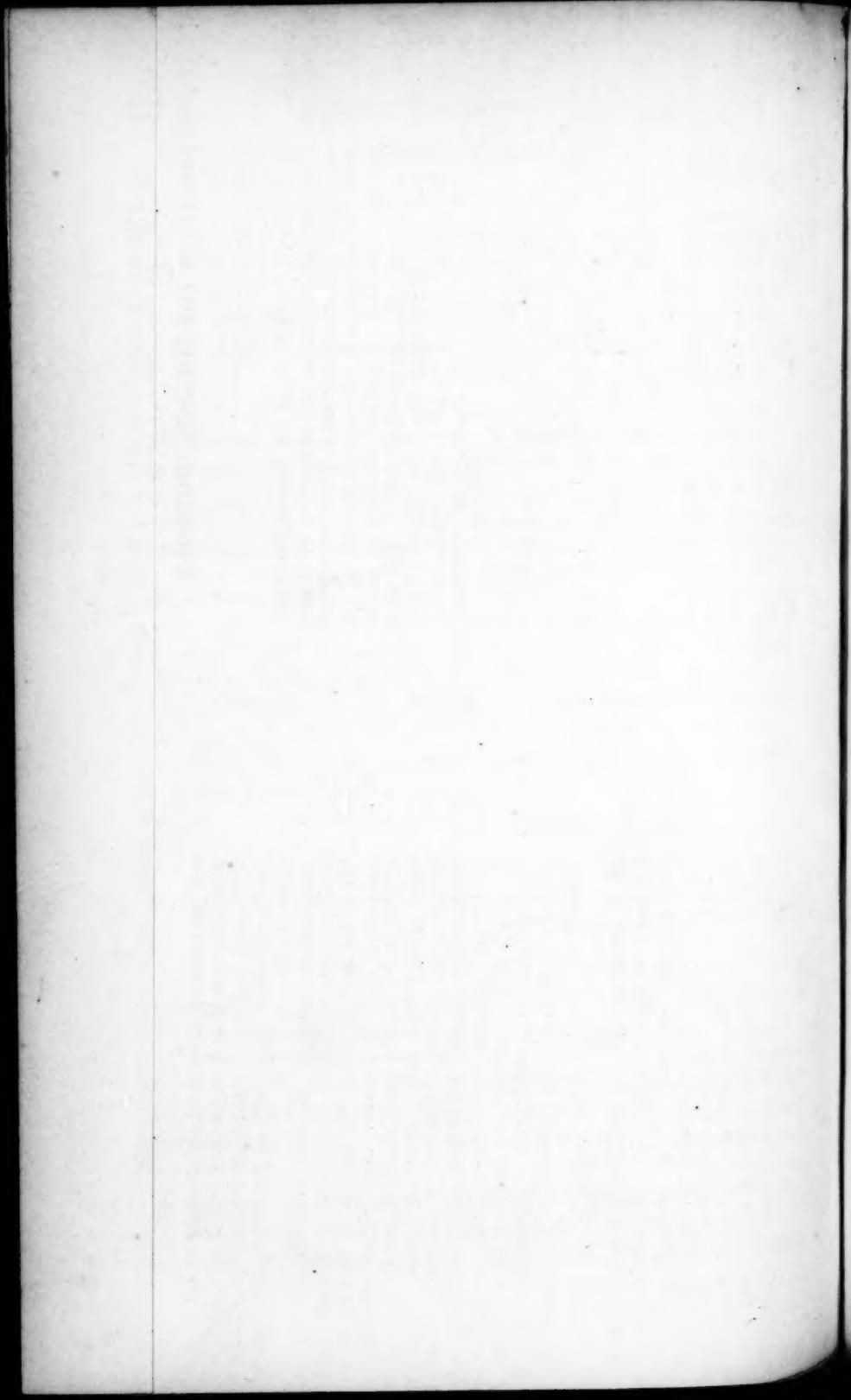
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	Muriates.			Sulphates.			Carbonates.				Oxide of iron.	Hydrobromate of soda.	Hydrodate of soda.	Solid contents grains in a gallon.	Free carbonic acid gas. Cubic inches in a gallon.	Free hydro-sulphuric acid gas. Cubic inches in a gall.	Authority for the analysis.	
	Soda.	Lime.	Magnesia	Soda.	Lime.	Magnesia	Soda.	Lime.	Magnesia	Iron.								
<b>MONTPELLIER SPA.</b>																		
No. 1. Saline chalybeate .	216.00	..	..	117.60	10.4	32.0	8.80	..	..	..	2.4	a trace	a trace	387.20	20.	..	Cooper.	
No. 2. Ioduretted and sulphurated saline .	282.4	..	..	227.20	24.8	57.6	..	..	..	..	3.36	..	1.2	596.56	3.2	12.8	..	
No. 4. Pure saline .	419.2	..	..	137.6	21.6	113.6	9.6	8.8	..	..	..	a trace	a trace	710.4	11.2	..	..	
No. 4 A. Strong ioduretted saline .	411.2	66.4	60.0	112.0	16.8	136.8	19.2	25.6	..	..	..	..	..	2.0	850.00	12.8	..	..
No. 5. Ioduretted magnesian saline .	77.60	104.8	84.0	..	24.8	376.0	13.6	..	..	..	3.2	a trace	2.80	686.80	9.6	..	..	
<b>PITTVILLE SPA.</b>																		
No. 1. Strong saline .	217.28	..	..	140.40	7.12	..	..	1.6	..	..	..	1 grain of bromine in 6½ gall.	a trace	366.4	..	..	Daubeny.	
" "	388.8	..	..	161.6 cryst}	..	44.0	44.8	8.	..	..	..	a trace	..	647.2	8	..	Daniel.	
" "	344.	..	..	160.0	..	40.0	40.0	16.	..	..	..	.24	a trace	600.24	..	..	Buckman.	
<b>ROYAL OLD WELLS.</b>																		
No. 1. Original Old Well .	465.60	49.68	20.32	116.08	..	..	..	..	..	..	a trace	..	..	652.08	1.10	3.53	Scudamore.	
No. 2. Sulphuretted saline .	180.80	29.44	41.28	418.56	..	..	..	..	..	..	a trace	..	..	670.08	1.15	4.60	..	
No. 3. Strong chalybeate saline .	140.80	24.64	26.40	345.6	..	..	..	..	..	..	a large proportion	..	..	537.44	1.5	1.35	..	
No. 4. Pure saline .	390.40	34.32	58.40	473.6	..	..	..	..	..	..	a trace	..	..	956.72	..	..	..	
No. 6. Strong muriatic saline .	776.0	..	..	29.6	116.0	99.2	..	12.8	..	..	..	..	..	1033.6	a large quantity	..	..	
Cambray chalybeate .	24.00	15.5	9.0	..	..	..	8.95	7.05	..	..	..	..	..	64.50	24.	Accum.		
Sulphur spring .	280.0	..	..	188.0	9.6	40.0	..	..	..	..	2.4	..	..	520.0	12.0	20.0	Brande & Parkes.	
Pure saline .	400.0	..	..	120.0	36.0	88.0	..	..	..	..	..	..	..	644.0	..	..	..	
Chalybeate .	330.4	..	..	181.6	20.0	48.0	4.0	..	..	..	6.4	..	..	590.4	20.	..	..	

**REMARKS.** No. 5. Royal Old Wells. This water contains saline constituents, similar to No. 2, and also a proportion of carbonate of iron. It contains, besides, a large impregnation of hydro-sulphuric acid, but little inferior to that in the Harrowgate waters. This water and No. 2, should be drank immediately at the pump, when pumped up, as the hydro-sulphuric acid rapidly disappears, if not taken directly. No. 6. This water contains a nitrate and salt of potash in very small quantities, and also a trace of silex.—J. SCUDAMORE.

[To face page 212.



May 15, 1848.

The President in the Chair.

Gilbert F. Matheson, Esq., Robert Mushet, Esq., Adam Birkmyre, Esq., A. W. Williamson, Ph. D., and Edward Chambers Nicholson, Esq., were elected Members of the Society.

The following papers were read :

XVIII.—*On the composition and origin of Condurrite.* By J. BLYTH, M.D., Royal Agricultural College, Cirencester.

In the Philosophical Magazine for 1827, the description of a mineral found in the Condurrow mine, near Camborne, in Cornwall, is given by Phillips, on which he bestowed the name of Condurrite.

It was found in one mass, weighing a few hundred pounds, 65 fathoms under the surface of the Condurrow mine, "alone in the vein, or rather unmixed with other metallic ores : beside it lay a mass of native copper, and much yellow copper ore, at a distance from it on the east in the vein ; about 8 fathoms above it, was found a small quantity of grey copper ore." The general colour of the new mineral was brownish-black, presenting sometimes a tinge of blue. It soiled the fingers, was brittle, yielded to the knife which produced a polished metallic-looking surface, nearly of a lead-grey colour.

The mineral was analyzed by Faraday, who found it to consist in 100 parts of

Water . . . . .	8·987
Arsenious acid . . . . .	25·944
Alloy { Copper . . . . .	60·498
Sulphur . . . . .	3·064
Arsenic . . . . .	1·507
Trace of iron . . . . .	
	100·000

The singularity of its composition, and the opinion expressed by Faraday that the substance was only a mechanical mixture, induced me to repeat its analysis.

To the kindness of Mr. Warington and Mr. Tennant, I am indebted for the very fine specimens which were put at my command for this purpose. The investigation was commenced a very considerable time ago—but my continued occupation in teaching, obliged me to abandon its further prosecution till lately.

In the meantime, the analyses of Rammelsberg and Kobell having appeared, and differing materially from the results which I had

obtained, I resumed the subject at the first moment of leisure. For several of the following analyses, I am indebted to my assistant, Mr. Thomas Towell.

A careful examination soon convinced me of the correctness of Faraday's supposition, and that the mineral was indeed a mixture.

The specimens analyzed by me were amorphous masses, of a brownish-black colour, very brittle, and readily soiling the fingers. When cut with a knife, or rubbed with a hard substance, the brown mass assumes a polished appearance. Some specimens were mixed with foreign matter disseminated through the mass. The purer portions consisted of nodules of a uniform brownish-black colour, presenting on different points of the surface an extremely thin layer of yellowish-looking substance, which, in very minute quantity, was found more uniformly spread between the nodules, to which it formed a kind of cement. On dissolving the smaller nodules in nitric acid, and filtering, the surface of the filter was frequently tinged with this substance. The interior of the larger compact masses was quite free from it.

The specific gravity of the mineral varied in different specimens from 4.29—4.20.

On charcoal before the blow-pipe, abundant vapours of arsenious acid were evolved, and a metallic globule of the colour of copper was left.

Heated in a long narrow tube, closed at the end, the mineral gave off water and a sublimate of arsenious acid, leaving brilliant metallic copper as a residue. The same appearances were presented on heating the mineral in a tube in an atmosphere of carbonic acid gas. Water extracted arsenious acid. Boiled with caustic potash, the filtrate, when neutralized with nitric acid, gave, with nitrate of silver, the brown precipitate of arseniate of silver, and the residue contained suboxide of copper.

Boiled with a solution of carbonate of soda, filtered and neutralized with nitric acid, the filtrate yielded a yellow precipitate of the arsenite of silver.

When the powdered mineral is treated with cold strong hydrochloric acid and rapidly filtered, it gives with ferrocyanide of potassium a whitish precipitate, of a rosy tint, rapidly passing into a deeper shade of the same colour, and becoming finally brown. Filtered into water, a white precipitate is produced. If the solution, however, be exposed for a short time to the air, no effect is produced by the addition of water, and ferrocyanide of potassium affords a brown precipitate.

If boiling hydrochloric acid be employed, the same indications of suboxide of copper are obtained. In this case, the precipitate obtained by ferrocyanide of potassium is at first of a purer white than that obtained from the cold hydrochloric acid solution.

The composition of the insoluble residue depends on the length of time the boiling with hydrochloric acid has been continued. If this has not been protracted, the residue consists of sulphur, copper, iron and metallic arsenic.

By continued boiling, the whole of the copper, iron and sulphur disappear, leaving metallic arsenic alone, which in its turn, by continuing the operation, is also dissolved.

The qualitative examination, therefore, indicated the presence of an oxidized and a non-oxidized portion; the former consisting essentially of arsenious acid and suboxide of copper, with a small admixture of oxide of copper; the latter, of sulphides of copper and iron and of arsenide of copper.

From the analyses of Faraday, Kobell considered the chief portion of the mineral to be an arsenite of copper, having the formula



He takes no account, however, of the unoxidized portion.

Although many minerals are known, containing arsenic acid as one of their component parts, yet arsenious acid has not been distinctly ascertained to belong to the field of mineralogy. The arsenious acid found in the Hartz, with the ores of silver, arsenic and lead, is probably only a product of decomposition.

The only instance of an arsenite formally given in mineralogical works, is that of a variety of cobalt bloom, which on being heated in a tube, gave a sublimate of arsenious acid, and was supposed to be an arsenite of cobalt. Recent investigations of Kersten,\* however, have shown that this was not a chemical compound, but a mere mixture of cobalt bloom (arseniate of copper) and arsenious acid, as the latter substance could readily be extracted by water.

The qualitative examination likewise proved this to be the case with condurrite.

- I. 0·529 grms. of condurrite treated with boiling water, and the arsenic determined by precipitation with sulphuretted hydrogen, the sulphur being oxidized by fuming nitric acid, gave arsenic = 0·050.
- II. 0·660 grms. gave 0·065 arsenic.

\* Pogg. An. LX. p. 262.

The quantity of arsenious acid per cent dissolved by water, was :

I.	II.
12·47	13·01

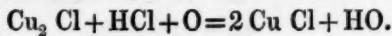
The view advanced by Thomson appears to be more probable than that of Kobell. Condurrite, according to the former chemist, is derived from a substance which contained originally one atom of sulphide and three of arsenide of copper. The average per centage of sulphide of copper found in the various analyses, might seem to support this view. In this case, however, sulphide of iron must also be reckoned as one of the ingredients, as its amount is as constant as that of the sulphide of copper. If, however, we admit these abundantly-occurring sulphides to be merely admixtures, then the original form of condurrite may be regarded as an arsenide of copper, from which the actual mineral is derived by partial oxidation.

It is scarcely possible to ascertain exactly the composition of the original arsenide by the analysis of either the oxidized or non-oxidized portion separately. In the former case, the constituents not being in chemical combination, and one of them possessing a certain degree of solubility in cold water, the composition will vary according as the mineral has been more or less exposed to the action of this agent. The non-oxidized portion, on the other hand, is so much influenced by the mode of treatment adopted, that it cannot be regarded even as an approximation to the composition of the original arsenide.

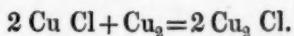
From the slight degree of solubility of metallic copper in hydrochloric acid, this reagent appeared to be the best means of separating the two portions of the mineral from each other. There is, however, great difficulty in dissolving out the whole of the arsenious acid by cold hydrochloric acid, and the employment of heat is quite inadmissible.

The quantity of copper dissolved by the boiling acid, and the composition of the insoluble matter, depends entirely on the length of time during which the action has been continued.

If finely-divided metallic copper, formed by the reduction of oxide of copper by hydrogen gas, be boiled with hydrochloric acid, a small portion is dissolved as subchloride, forming a colourless solution, which, on exposure to the air, becomes of a yellowish-green, by conversion into the chloride



On boiling this chloride with the metallic copper, it is again reduced to the state of subchloride,



The same reaction takes place with arsenide of copper.

Thirteen grains of copper, obtained by reducing the oxide with hydrogen gas, was intimately mixed with five grains of metallic arsenic, perfectly free from all trace of arsenious acid, and introduced into a piece of combustion tube, narrowed in diameter at both extremities.

A stream of hydrogen gas was passed through the tube for some time, and both ends being carefully sealed by the blow-pipe, whilst still full of the gas, the two metals were made to combine at a comparatively low temperature. The arsenide thus formed was of a steel-grey colour, and could be readily pulverized.

On boiling this compound in hydrochloric acid, a small portion was dissolved, forming a colourless solution, which became of a yellowish-green on exposure to the air. In the colourless solution, potash produced a yellowish precipitate; ferricyanide of potassium, a brown; and ferrocyanide, a white, which rapidly assumes a rose, and finally a brown colour.

The yellowish-green solution gave the reactions of oxide of copper alone.

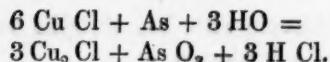
By repeatedly boiling and cooling, the arsenide was at last entirely dissolved. If oxide of copper be added during the operation, the solution of the arsenide takes place much more rapidly.

If arsenide of copper in excess be boiled with a solution of chloride of copper (made by dissolving oxide of copper in an excess of hydrochloric acid, and filtering), the latter is entirely reduced to the state of subchloride. On adding another portion of the solution of the chloride, and again boiling, the arsenide is rapidly dissolved. The same reactions are produced with condurrite by a similar solution.

The arsenic, as well as the copper, in the above experiment, takes part in the reduction.

A portion of metallic arsenic, perfectly free from arsenious acid, boiled for five minutes in a small quantity of the solution of chloride of copper, produced a colourless liquid, which gave the reactions of the suboxide alone.

To a portion of the fluid, after boiling and cooling, nitrate of silver and nitric acid were added, and the chloride of silver was separated by filtration. The filtrate, carefully neutralized with ammonia, gave the brown-coloured arseniate of silver.



Rammelsberg found, on separating the soluble from the insoluble portion by boiling hydrochloric acid, the proportions of copper and arsenic in the latter to be :

Subsulphide of copper (Cu <sub>2</sub> S) . . . . .	= 10·85
Copper . . . . .	= 4·16
Arsenic . . . . .	= 13·89

Kobell states that "the residue found by him, after the same treatment, consisted of finely-divided metallic arsenic."

The composition of this residual matter, however, appears to have depended on the length of time the boiling was continued. In all the preceding experiments on the solution of the artificial arsenide by means of a solution of chloride of copper, the copper was always found to be much more rapidly dissolved than the arsenic. A portion of condurrite, which had been boiled with hydrochloric acid for the purpose of determining the composition of the insoluble portion, was forgotten for some days on the sand-bath. On filtering and dissolving in nitric acid, the residue, which was very small in quantity, was found to consist of arsenic alone, without a trace of copper.

The relative proportions of copper and arsenic in the residual arsenide, given by Rammelsberg, from which he deduces the formula



and from the oxidation of which condurrite may be supposed to have been derived, must have been materially changed by the boiling hydrochloric acid.

A good mode of effecting the separation of the two portions of the mineral, without the employment of hydrochloric acid, is by carbonate of ammonia.

5·065 grms. of finely-pounded condurrite were digested for 20 minutes in a strong solution of carbonate of ammonia, thrown on a weighed filter and rapidly washed with a solution of carbonate of ammonia till the filtrate came through colourless.

The insoluble matter left, amounted to 0·089 grm. = 17·57 per cent.

The proportion of the soluble to the insoluble portions is as was to be expected, in no two cases the same.

0·272 grm., treated in the same way, left

insoluble matter . . . . . 0·0333 = 12·13 per cent

0·4175 „ left. . . . . . . . . 0·101 = 24·19 „ „

The analysis of the soluble and insoluble portions of 0·5065 grms., separated by carbonate of ammonia, gave, for the soluble portion :

$$\text{Copper} = 0\cdot225$$

$$\text{Arsenic} = 0\cdot080$$

for the insoluble (=0·089) :

$$\text{Copper} = 0\cdot058$$

$$\text{Arsenic} = 0\cdot014$$

$$\text{Iron} = 0\cdot002$$

$$\text{Sulphur} = 0\cdot014$$

$$\underline{0\cdot088}$$

The relation between the arsenic and copper, in 100 parts of the soluble and insoluble portions, cannot be ascertained by direct calculation after separating the two by carbonate of ammonia.

The soluble portion contains other matters besides the copper and arsenic; and in the insoluble, sulphide of iron and copper are invariably present. The relative quantities have therefore been calculated upon one hundred parts, after deducting the non-essential substances, and regarding the copper and arsenic as forming an arsenide.

In the portion dissolved by carbonate of ammonia, the following quantities of copper and arsenic were found :

$$\text{Copper} = 0\cdot225$$

$$\text{Arsenic} = 0\cdot080$$

In 100 parts :

$$\text{Copper} = 73\cdot74$$

$$\text{Arsenic} = 26\cdot23$$

In the insoluble portion, if the iron is supposed to exist as sesquisulphide ( $\text{Fe}_2 \text{S}_3$ ), and the copper as subsulphide ( $\text{Cu}_2 \text{S}$ ), then the quantity of sulphur necessary for combining with 0·002 of iron is 0·0017, leaving 0·012 for the copper.

The quantity of copper necessary to form subsulphide ( $\text{Cu}_2 \text{S}$ ), corresponding to 0·12 parts of sulphur, is 0·047.

$$\text{Total copper in insoluble portion} = 0\cdot058$$

$$\text{Copper united to sulphur} . . = 0\cdot047$$

$$\text{Copper united to arsenic} . . = \underline{0\cdot011}$$

In the insoluble portion, the arsenic and copper supposed to exist as an arsenide are, therefore,

$$\text{Copper} = 0\cdot011$$

$$\text{Arsenic} = 0\cdot047$$

In 100 parts :

Copper = 44.00

Arsenic = 56.00

The copper and arsenic, therefore, in the oxidized and non-oxidized portion, bear no relation to each other.

The residual matter left by the carbonate of ammonia cannot be taken as truly representing the composition of the original arsenide. Were this the case, the arsenic and copper must have undergone oxidation with equal rapidity, and the proportions of these two substances must have been found the same in the oxidized and non-oxidized portion, as in the original compound.

A more probable method of arriving at an approximation to the real composition of the original arsenide, appears to be by the assumption, that the whole of the arsenic and copper have existed in direct combination, with the exception of the portion of copper which is found as sulphide.

There is, however, one source of error in this mode of calculation, arising from the probable loss of a portion of the arsenious acid by the action of water, which would thus give rise to an arsenide containing less arsenic than originally existed.

If the sulphides present be the most commonly occurring compound,  $\text{Cu}_2\text{S} + \text{Fe}_2\text{S}_3$ , no error would be introduced into the calculation by their oxidation, unless we suppose  $\text{Cu}_2\text{S}$  becomes  $\text{CuO}$  and  $\text{CuO SO}_3$ , or that  $\text{Cu}_2\text{O}$  and  $\text{SO}_3$  are first formed, and then change immediately into  $\text{Cu}$  and  $\text{CuO SO}_3$ . In these cases, by the removal of the sulphate by water, the calculation would give an arsenide, having more copper than the original compound. As the general products of the oxidation of the different sulphides of copper and of iron, are, however, in the first instance, salts of the protoxides of these metals,  $\text{Cu}_2\text{S} + \text{Fe}_2\text{S}_3$  would become  $2\text{CuO SO}_3 + 2\text{FeO SO}_3$ , and either be entirely dissolved out; or if they remain, the calculation would easily indicate the quantity of copper existing originally as sulphide, if the whole of the sulphur oxidized, as well as the unoxidized, be estimated at once.

By treating from two to three grammes of the interior portions of a compact specimen of condurrite with cold water, rapidly filtering and adding chloride of barium, and hydrochloric acid, only the very faintest opalescence was perceived. The quantity of sulphuric acid present, therefore, is totally inappreciable by weight.

It is probable, therefore, that the great solubility of the sulphates of copper and of iron, if present only in small quantities, allowed of their rapid removal by the action of water before any appreciable loss of arsenious acid took place from the same cause.

In the following analyses, the interior portions of the hardest and most uniform specimens were selected. The numbers obtained can, however, be regarded in the light of approximations only to the truth.

I. 1·665 grm. of condurrite, selected from the interior of a hard uniform nodule, gave when analyzed by nitro-hydrochloric acid :

Metallic copper	= 0·9605
Arsenic . . .	= 0·369
Iron . . .	= 0·0057
Sulphur . . .	= 0·037

A second portion, from the interior of another large nodule, apparently uniform in composition, was fused with carbonate of soda and nitrate of potash. The arsenic acid was separated by water, reduced by sulphurous acid to arsenious acid, and the latter precipitated by sulphuretted hydrogen, and the sulphur oxidized, gave in

II. 0·500 grm.

Copper	= 0·285
Arsenic	= 0·1128

III. The total amount of copper, arsenic, iron and sulphur in 0·5065 grm. given at page 249, are :

Copper	= 0·283
Arsenic	= 0·094
Iron	= 0·002
Sulphur	= 0·014

IV. From the same specimen as No. I. 1·4235 grm. gave :

Copper	= 0·8335
Iron	= 0·0043

V. 0·7235 grm. gave :

Copper	= 0·4013
Iron	= 0·0024

VI. Arsenic determined from the same specimen as No. V.

0·745 grm. gave :

Arsenic = 0·1294

VII. 0·5785 grm. gave :

Copper	= 0·344
Arsenic	= 0·1117
Iron	= 0·002

VIII. 0·48 grm. gave :

Copper	= 0·292
Arsenic	= 0·0954
Iron	= 0·0007

IX. 0·489 grm. gave :

Copper = 0·296

Arsenic = 0·0954

Iron = 0·0001

The last three portions (7, 8, 9,) were taken from the same large, very compact nodule.

Four determinations of sulphur, taken from 2, 5 and 7, gave as the quantities of sulphur per cent, 2·22, 2·475, 2·314, 2·70; mean 2·42.

The mean quantity of iron from the same specimens, was, in five analyses 0·37 per cent.

The preceding analyses, calculated for 100 parts, will stand thus :

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
									mean	mean
Copper = 57·65	57·00	55·87	58·55	55·47	—	59·44	60·83	60·53	—	—
Arsenic = 22·22	22·56	18·56	—	—	17·37	19·30	19·88	19·35	—	—
Iron = 0·34	—	0·41	0·305	0·33	—	0·399	0·147	0·21	—	0·37
Sulphur = 2·22	—	2·75	—	—	—	—	—	—	2·42	—

Faraday's analysis, (p. 213), will yield the following per centage, when the different substances are calculated in their uncombined state:

Copper = 60·498

Arsenic = 21·16

Sulphur = 3·064

Iron, a trace, (mean, found as above, 0·37).

In the preceding analyses the same specimen was employed in Nos. 1 and 4; a second specimen for No. 2; a third for No. 3; a fourth for Nos. 5 and 6; and a fifth for Nos. 7, 8 and 9. In those cases where no arsenic, sulphur or iron is given, they are taken, for the purposes of calculation, from the preceding analysis, if the two happen to be made from the same specimen; otherwise the mean quantity of sulphur and iron found, is assumed as the basis of the calculation.

By deducting from the total quantity of copper in each case, that portion which exists as  $\text{Cu}_2\text{S} + \text{F}_2\text{S}_3$ , the arsenic and copper will then stand in the following relation to each other :

I.	II.	III.	IV.	V., VI.	VII.	VIII.	IX.
Copper = 50·05	48·69	46·38	50·80	47·04	51·21	51·77	51·67
Arsenic = 22·22	22·56	18·56	22·22	17·37	19·30	19·88	19·35

Calculated for 100 parts :

I.	II.	III.	IV.	V., VI.	VII.	VIII.	IX.
Copper = 69·25	68·33	71·42	69·57	73·03	72·62	72·25	72·75
Arsenic = 30·74	31·66	28·58	30·43	26·96	27·37	27·74	27·24

The mean of the above is :

$$\begin{aligned}\text{Copper} &= 71\cdot 15 \\ \text{Arsenic} &= 28\cdot 84\end{aligned}$$

Faraday's analysis, calculated in the same manner, gives :

$$\begin{aligned}\text{Copper} &= 70\cdot 11 \\ \text{Arsenic} &= 29\cdot 88\end{aligned}$$

These quantities correspond to an arsenide containing 6 equivalents of copper and one of arsenic,



in which the amount of copper and arsenic per cent are :

$$\begin{aligned}\text{Copper} &= 71\cdot 69 \\ \text{Arsenic} &= 28\cdot 30\end{aligned}$$

and which is identical in composition with an arsenide of copper from Chili, analyzed by Domeyko,\* and which was found at a considerable depth in a mine of native silver and oxide of copper, replacing these two bodies.

It occurred in veins of about three lines in thickness. "It is amorphous, compact or granular, and possesses metallic lustre. The colour of the fresh fracture resembles that of the pure native arsenide of iron; it is, however, much more brilliant than the latter, and possesses a yellowish tint, which finally becomes deeper on prolonged exposure to the air." The fracture is irregular, and sometimes imperfectly conchoidal. It takes a polish like silver when cut by the knife. The minerals which accompany it are the arseniate and the suboxide of copper. The black oxide is never found with these arsenides."†

The purer specimens Domeyko found to consist in 100 parts of :

$$\begin{aligned}\text{Copper} &= 71\cdot 65 \\ \text{Arsenic} &= 28\cdot 36\end{aligned}$$

Another specimen from the mine of San Antonio, in the district

\* The arsenide of copper, either pure or mixed with copper pyrites, is found "dans une seconde chaîne de filons cuivreux beaucoup plus rapprochée du centre des Cordillères. Leur gisement est déjà dans le même terrain secondaire stratifié auquel se rapportent les mines d'argent : les roches sont presque toujours des porphyres stratifiés alternant avec des brèches et schistes porphyroïdes."—*An. des Mines*, 4ème Sér., III. p. 3.

† *An. des Mines*, 4ème Sér., III. p. 9.

Copiao, in Chili, was found to be mixed with the same sulphides as condurrite, and consisted of :

Copper	=	61·93
Arsenic	=	20·39
Iron	=	0·46
Sulphur	=	3·39
Matrix	=	12·39
		98·56

Deducting the non-essential parts, the composition per cent is the same as that of the purer specimen—viz. :

Copper	=	71·00
Arsenic	=	27·00

Accompanying these ores, native copper was likewise found, containing, in some cases, from 4 to 5 per cent of arsenic.

The first discoverers of condurrite found a specimen of a mineral about the size of a walnut in contact with it, which in some points resembles the arsenide of Domeyko. It consisted of “a tin-white metallic substance, which is hard, but yields to the knife, and is extensible under the hammer. It is coated by the black ore (condurrite) and is accompanied by native copper, which is even in some places intermingled with it, as may be seen with the assistance of a glass, on viewing a surface produced by the knife : by exposure, this surface becomes yellow.”\* This substance, when heated in a green glass tube, was found by Faraday to give out arsenious acid. “The quantity was, however, small, and the rest of the mineral fused at a red heat into a substance, which, when cold, was brittle, grey, and by examination, proved to consist of copper and arsenic, in combination with a small quantity of sulphur, and a trace of iron.”

It remains to be seen if further careful examination of the Condurrow mine will reward the investigator with the discovery of an arsenide of copper having the composition which has been indicated in the preceding pages.

*Appendix.*—Besides copper, arsenic, iron and sulphur, condurrite contains a considerable portion of water, which can only be removed by a temperature of 212° Fahr., and a quantity of nitrogenized organic matter, which is in a state of intimate admixture with every portion of the mineral. The quantity of oxygen present is, singularly enough, just sufficient to oxidize the whole of the arsenic and organic

\* Phil. Mag., Oct. 1827, p. 287.

matter, and a small portion of the sulphur. The water was determined by heating a portion of the finely-powdered mineral in a Liebig's drying-tube, at  $212^{\circ}$  Fahr. To prevent any portion of the arsenious acid from being carried away by the vapour of the water, both the horizontal and perpendicular portions of the wide limb of the tube were loosely packed with cotton, and for control, were connected with a chloride of calcium tube, and with an aspirator. The atmospheric air was admitted by the narrow limb, after being thoroughly dried by passing through strong sulphuric acid and a long tube filled with chloride of calcium.

I. A portion (2·06 grms.) of the mineral, previously dried for several days over strong sulphuric acid under the air-pump, until the weight remained unchanged, lost only  $0\cdot011 = 0\cdot534$  hygroscopic water per cent.

II. 1·0845 grm. of fresh mineral, heated in Liebig's tube, as above described, until the weight remained unchanged, lost  $0\cdot027$  (corresponding to the increase of weight of the chloride of calcium tube) = 2·49 water per cent.

III. 0·7315 grm., treated in the same manner, lost  $0\cdot017 = 2\cdot33$  per cent. of water.

This quantity of water appears much smaller than that obtained by Faraday; viz., 8·987 per cent. A portion of this is, however, derived from the organic substance, as the following analysis, in which the arsenious acid and water were determined together, will shew.

A portion of the mineral, finely divided, was introduced into a piece of combustion-tube, narrowed in diameter at both ends. One extremity was connected with an apparatus for the evolution of carbonic acid, a long tube filled with chloride of calcium and a bottle of strong sulphuric acid being interposed between the combustion-tube and evolution-bottle. The other extremity passed through a cork into a tube ten inches long, loosely packed with carefully dried asbestos, to which a chloride of calcium apparatus and an aspirator were attached.

The atmospheric air was first completely expelled by the dry carbonic acid gas, and the combustion-tube then heated by the strongest flame of a Berzelius' lamp. At the conclusion of the combustion, the water was removed from the arsenious acid by allowing the current of warm, dry carbonic acid to pass through the apparatus for a considerable time. The asbestos and chloride of calcium tube, weighed before and after the operation, gave the amount of arsenious acid and water.

I. 0·5785 grm. treated as above described, gave :

Water = 0·046 ; Arsenious acid \* = 0·1475.

The residue in the combustion-tube after the operation, amounting to 0·347 grm., was dissolved in fuming nitric acid, and found to consist of metallic copper and iron, with a mere trace of sulphur. The two metals, separated by sulphuretted hydrogen and weighed as oxides, gave :

Oxide of copper	=	0·432	=	0·344	metallic copper
Peroxide of iron	=	0·0033	=	0·002	„ iron
Sulphate of barytes	=	0·023	=	0·003	sulphur
				0·349	

II. 0·48 grm. treated as before, gave :

Water = 0·045 ; Arsenious acid = 0·126.

The residue, as before, contained only a trace of sulphur, and consisted of copper 0·292 ; iron = 0·0007.

III. 0·489 grm. gave :

Water = 0·039 ; Arsenious acid = 0·125.

The residue = 0·298, contained iron = 0·001 ; copper = 0·296, and a trace of sulphur.

These analyses calculated for 100 parts, yield :

	I.	II.	III.
Copper . . .	= 59·44	60·83	60·53
Arsenic . . .	= 19·30	19·88	19·35
Iron . . .	= 0·39	0·14	0·21
Water driven off at 212°	= 2·41	2·41	2·41
Water from organic matters	= 5·54	6·96	5·66

The complete reduction of the suboxide of copper to the metallic state in the preceding analyses is partly due to the arsenic and sulphur, as well as to the organic matter present.

On heating a mixture of oxide of copper and metallic arsenic or arsenide of copper, in a tube, in an atmosphere of dry carbonic acid,

\* The arsenious acid, being dissolved in water, acidulated with hydrochloric acid, and determined as sulphide, was found to correspond exactly to the quantity indicated by the increase of weight in the tube containing the asbestos.

arsenious acid is formed, and the oxide of copper is first reduced to the state of suboxide, and finally to the metallic state.

To ascertain the amount of organic matter, a portion of the mineral was submitted to combustion.

I. 2·046 grms. burned with chromate of lead and copper turnings, gave:

Carbonic acid = 0·121; Water = 0·132.

II. 2·13 grms. burned in the same way, gave:

Carbonic acid = 0·127; Water = 0·136.

III. 2·881 grms. gave, according to Will and Varrentrapp's method, 0·026 of the double salt of platinum and ammonium = 0·0573 per cent of nitrogen.

Deducting the hydrogen (0·267), corresponding to the mean amount of water per cent (2·41), driven off at 212° Fahr., and calculating the remainder as belonging to the organic matter, the composition will stand thus:

	I.	II.	III.
Carbon . . . . .	1·613	1·626	—
Hydrogen . . . . .	0·449	0·442	—
Nitrogen . . . . .	—	—	0·057

Taking the mean amount of copper, arsenic and iron of the last three analyses, the sulphur and water of former determinations, and the organic matter just given, the true composition of condurrite in 100 parts will be:

Copper . . . . .	= 60·21	
Arsenic . . . . .	= 19·51	
Iron . . . . .	= 0·25	
Sulphur . . . . .	= 2·33	
Water { driven off at 212° }	= 2·41	
Carbon . . . . .	= 1·62	
Hydrogen . . . . .	= 0·44	organic matter
Nitrogen . . . . .	= 0·06	15·29
Oxygen . . . . .	= 13·17	
		—
	100·—	

Some very large nodules of this mineral, which had been washed with water to remove adhering impurities, were placed for two hours in the sun to dry, and then packed in a box. Two days afterwards, the box was found burst in all directions, and on unpacking the contents, Mr. Talling, of Lostwithiel, Cornwall, (to whom, through Mr.

Warington, I am indebted for this curious observation), found on examination, that the large nodules of condurrite were so hot, as scarcely to allow of their being held in the hand. The heat of the smaller nodules was in proportion to their size. The largest specimens remained in this state for two or three days after exposure to the air: a great quantity of moisture had also been deposited on the other contents of the box. It is probable that, by the combined action of the oxidation of the sulphide and arsenide a sufficiently high temperature may have been developed, possibly much greater than that observed by Mr. Talling, which would account for these curious facts.

From the preceding analyses, it is evident that sufficient organic matter and water are present, if converted suddenly into a gaseous state by heat, to explain the observed phenomena.

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XIX. *Artificial formation of Urea from Fulminic Acid.* By J. H. GLADSTONE, PH. D.

During the investigations of Professor Liebig upon fulminic acid, he was led to believe, that urea was formed when the fulminate of copper and ammonia was decomposed by sulphuretted hydrogen. A statement to that effect is to be found in the "Lancet" of Dec. 7th, 1844; but the fact was never established by satisfactory experiment. The discovery of Wöhler, that urea may be artificially produced from cyanic acid and ammonia, rendered this transformation of fulminic acid antecedently probable, upon the supposition of the isomerism of the two acids: since, however, this has been disputed, it became desirable to resume an inquiry so interesting and important in a theoretical point of view.

Fulminating silver was prepared in the manner recommended by Geiger; *i. e.* one part of metallic silver was dissolved in 10 parts of nitric acid, sp. gr. 1.36, and the solution was poured into 20 parts of alcohol, sp. gr. 0.85. The mixture was heated until nitrous ether was formed with considerable ebullition, and then, the heat being removed, was allowed to remain till the solution became troubled, and fulminating silver was deposited in crystals. The salt thus prepared was well washed by decantation, and set aside in a warm place with metallic copper, in vessels containing a large amount of water. By this means the silver was wholly precipitated, while copper entered into combination with the fulminic acid, forming a salt, which remained in solution. The liquid was then poured off, and treated with a large excess of

ammonia, by which one of the atoms of metal in the fulminate of copper was displaced, and ammonia substituted. Through this solution of fulminate of copper and ammonia, sulphuretted hydrogen was passed, until it ceased to produce a precipitate. The sulphuret of copper was separated by filtration, and the solution that resulted, containing sulphuret of ammonium, free ammonia, and the products of decomposition, was evaporated. During this process, a little sulphuret of copper and suboxide of copper separated, and afterwards a greyish powder, which, when decomposed by acid, yielded suboxide of copper, and an acid soluble in water, giving with a persalt of iron, the deep red tint, characteristic of sulphocyanogen. The solution filtered from this precipitate, and concentrated to a small bulk, gave crystalline precipitates with oxalic and nitric acids, closely resembling the salts which these acids produce with urea : in addition to this, a substance in combination with ammonia was obtained, which also gave the red colour peculiar to sulphocyanogen by the iron test.

In order to separate these two bodies completely, the following method was found efficacious. The solution was warmed with a quantity of hydrated oxide of lead, until all the ammonia was expelled : by this means the whole sulphocyanogen was precipitated as basic sulphocyanide of lead, and was separated by filtration. The resulting liquid still contained a trace of copper, which was removed by a little sulphuretted hydrogen, and the now colourless solution yielded, upon evaporation, crystals of apparently pure urea.

*Analysis of the urea.*—The urea was converted into oxalate, and burnt in the usual manner with chromate of lead. The following are the results of the analysis :

I. 0·4165 grm. of salt yielded 0·357 grm. carbonic acid, and 0·1825 grm. water.

II. 0·3345 grm. of salt purified by re-crystallization from water, yielded 0·2815 carbonic acid, and 0·146 water.

These numbers reckoned to 100 parts, and compared with those calculated from the formula of oxalate of urea  $C_2H_4N_2O_2, C_2O_3 + HO$ , afford :

	Calculated.	Found by experiment.	
		I.	II.
Carbon . . . . .	22·86	23·38	22·93
Hydrogen . . . . .	4·76	4·88	4·84
Nitrogen . . . . .	26·67	—	—
Oxygen . . . . .	45·71	—	—
	100·00		

An analysis of the nitrogen was also made by the differential method. Six tubes of mixed gases were collected, of which the 3rd, 4th, and 5th contained the following proportions :

Carbonic acid . . . . .	202	188	129
Nitrogen . . . . .	98	94	67

These numbers are very nearly as 2 : 1 ; the proportion in which the carbon and nitrogen exist in oxalate of urea.

*Analysis of the sulphocyanide.*—The mixture of oxide of lead and lead-salt, which was separated from the solution containing the urea, was decomposed by means of sulphuret of ammonium ; the sulphuret of lead was removed by filtration ; the solution, after being boiled to expel an excess of the reagent, was rendered acid with nitric acid, and nitrate of silver was added. This produced a copious white curdy precipitate, very susceptible of decomposition by light. The copper-salt, which separated during the first evaporation, was treated in a similar manner.

A weighed portion of the silver-salt was oxidized by means of strong nitric acid, and, when completely dissolved, the silver was precipitated by hydrochloric acid, and the sulphuric acid, afterwards, by chloride of barium. In this experiment 0·465 grm. of salt yielded 0·400 grm. of chloride of silver, and 0·6565 grm. of sulphate of barytes.

Another portion, weighing 0·573 grm. of the salt, purified by re-crystallization from ammonia, was burnt with chromate of lead, and yielded 0·1435 grm. of carbonic acid.

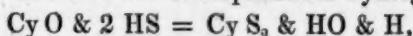
These numbers reckoned to 100 parts, and compared with those calculated from the formula of sulphocyanide of silver,  $\text{Ag}_2\text{C}_2\text{NS}_2$ , the nitrogen being estimated by the loss, afford :

	Calculated.	Found by experiment.
Silver . . . . .	65·06	64·80
Carbon . . . . .	7·23	6·83
Nitrogen . . . . .	8·43	8·90
Sulphur . . . . .	19·23	19·47
	100·00	100·00

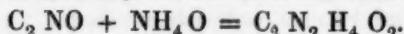
It thus appears that urea and sulphocyanide of ammonium are the products of the decomposition of fulminate of copper and ammonia by sulphuretted hydrogen ; and during the several repetitions of the experiment I observed no other product.

Upon the long-received view of the constitution of fulminic acid, the decomposition is easily explained. When the copper-salt is

decomposed, the one atom of acid, previously in combination with the metallic oxide, unites with two of sulphuretted hydrogen;



while the other atom of acid, that existed in combination with ammonia in the double salt, resolves itself into urea :



The whole decomposition may be thus expressed. One atom of fulminate of copper and ammonia, with three atoms of sulphuretted hydrogen, that is,  $\text{Cu O}$ ,  $\text{NH}_4 \text{O}$ ,  $\text{C}_4 \text{N}_2 \text{O}_2$  &  $3 \text{ HS}$ , are resolved into

1 at. of Sulphuret of copper . . . . .	Cu S
1 " Urea . . . . .	$\text{C}_2 \text{N}_2 \text{H}_4 \text{O}_3$
1 " Sulphocyanogen . . . . .	$\text{S}_2 \text{C}_2 \text{N}$
2 " Water . . . . .	$\text{H}_2 \text{O}_2$
1 " Hydrogen . . . . .	H
<hr/>	
$\text{Cu S}_3 \text{C}_4 \text{N}_3 \text{H}_7 \text{O}_4$	

It is probably owing to this atom of hydrogen, eliminated during the formation of sulphocyanogen, that I always found a considerable quantity of the oxide of copper reduced to the state of suboxide.

*On the action of oxalic acid upon the alkaline chlorides.* By ALFRED GEORGE ANDERSON.—When equivalent proportions of oxalic acid and chloride of sodium are dissolved together in hot water, the liquid crystals are formed on cooling. The mother-liquor becomes very yellow when concentrated, and contains free hydrochloric acid, oxalic acid and chloride of sodium. These crystals are freed from traces of chloride of sodium by re-crystallization.

- I. 16 grs. yielded, by strong ignition, 6·4 grs. of carbonate of soda.
- II. 30 " " 12·0 grs. carbonate of soda
- III. 15 " " by decomposition with chloride of calcium, 11 grs. of carbonate of lime.
- IV. 20 grs. afforded 14·45 carbonate of lime.

The following was, therefore, the composition of the salt :

		Calculated
Soda . . . . .	23·40	22·46
Oxalic acid . . . . .	51·87	51·69
Water . . . . .	24·73	25·85
<hr/>		<hr/>
	100·00	100·00

Agreeing with the formula,  $2 (\text{C}_2\text{O}_4) \text{NaO}$ , 4HO (binoxalate of soda).

This salt has been stated to be anhydrous, and composed of 9 acid + 4 base.

Equivalent proportions of oxalic acid and chloride of potassium, treated in the same way, yielded crystals on cooling the solution. The mother liquid resembles that obtained from the chloride of sodium, becoming yellow by concentration. The crystals are pure when re-crystallized.

I. 10 grs. afforded 2·65 grs. carbonate of potash.

II. 9 " " 2·40 grs. carbonate of potash.

The following was, therefore, the composition of the salt :

	Calculated
Oxalic acid . . . . .	56·66
Potass . . . . .	18·55
Water . . . . .	24·79
	<hr/>
	100·00

Formula 4 ( $C_2O_3$ )  $KO_7HO$ .

Equivalent quantities of chloride of ammonium and oxalic acid give rise to a similar reaction ; very beautiful crystals are obtained, which afford, by the usual mode of analysis, 86 per cent of carbonate of lime, agreeing in composition with the binoxalate of ammonia,  $2(C_2O_3) NH_4O_2 HO$ .

The quantity of the oxalate produced varies in all the cases, and seems to depend on the degree of concentration of the liquid. The decompositions are not, however, complete, in any one of the cases, even when proportions necessary for producing equivalents of each have been employed.

### Special Meeting, May 22, 1848.

The President in the Chair.

The following Report of the Council was read by the President :

At the annual meeting of the Society on the 30th of March, a motion was carried, recommending the Council to consider whether it would be for the interest of the Society, that steps should be taken for the purpose of procuring the grant of a Charter of Incorporation.

In pursuance of this recommendation, the Council has duly considered the subject, and is of opinion that it would be very desirable to obtain for this Society a Charter of Incorporation, provided the expenses attendant upon the necessary proceedings did not exceed such a sum as the Council felt justified in recommending the Society to expend for the purpose. The Council accordingly took such steps as have enabled them to ascertain that the entire outlay which will be incurred will not exceed the sum of £400. Under these circumstances, therefore, they have thought it right to summon the present meeting, with a view of com-

municating to the members the results of their inquiries, of ascertaining the opinion of the Society upon the subject, and of receiving their sanction in immediately taking final measures for procuring the said Charter of Incorporation, provided such should be the wish of the Society.

It was moved by Dr. G. D. Longstaff, seconded by George Smith, Esq., and resolved—That this meeting do authorize the Council to take the necessary steps for procuring a Charter of Incorporation, on the understanding that the expenses incurred by the funds of the Society do not exceed £400.

Resolved—That the Secretary be requested to prepare a list for receiving subscriptions to aid the funds of the Society in defraying the expences of the Charter, and that a circular letter be sent to the members, notifying the same and requesting their co-operation.

June 5, 1848.

The President in the Chair.

A specimen of the first piece of platinum consolidated in England from the spongy state, and also the first piece of platinum soldered with gold, by the late Mr. Thomas Cock, while at William Allen's, were presented by W. J. Cock, Esq., to the Society's museum.

Sir John Croft, Bart., was elected a member of the Society.

The following papers were read :

*On the phosphoric acid and fluorine contained in different geological strata.*  
By J. C. NESBIT, Esq. F.G.S.—The researches of Dr. Fownes and of Mr. Sullivan having proved the presence of phosphoric acid and fluorine in a great number of the older rocks, a series of analyses have been undertaken by Mr. Nesbit and his pupils, with a view to establish the presence of the same bodies in most of the sedimentary strata. The process of analysis employed, was essentially the same as that described in a paper read by Mr. Nesbit to the Society on January 17th, 1848,\* with certain modifications when large quantities of iron were present. With reference to the precautions that are necessary in estimating phosphoric acid, when fluorine is present, the following are the results of the author's experience.

"Having found traces of fluorine in some of the specimens, and considerable quantities in others, it became of importance to know, whether this substance was to be found in the precipitates of the pyrophosphate of magnesia, and on the examination of many pyrophosphate precipitates, the presence of fluorine was distinctly perceptible. The following experiments on the reactions of fluoride of calcium were therefore tried.

Fluoride of calcium, after repeated digestion with hydrochloric acid,

\* Journal of Chem. Soc. No. I. p. 44.

to remove the iron and alumina, was boiled with hydrochloric acid in a glass vessel. The hydrochloric solution, diluted with water, was mixed with acetate of soda. If the solution were not very dilute, a white precipitate, having exactly the appearance of phosphate of alumina or iron, made its appearance. If the solution were diluted still more, it became merely opalescent, and if sufficiently dilute, no precipitate was produced. But on boiling the solution, a white precipitate was produced, easily mistaken for phosphate of alumina or iron. This precipitate was soluble in hydrochloric acid, and if not too concentrated, was not re-precipitated on the addition of tartaric acid and ammonia in excess. But on shaking, either with or without the addition of the phosphoric acid test, a precipitate was produced if the solution was not very dilute.

The most singular properties of this precipitate are, its heavy crystalline character and the stellar form of the little crystals which, after some time, adhere to the sides of the glass; in fact, it closely resembles the phosphate of magnesia and ammonia.

From these experiments, it became apparent, that either the fluorine must be expelled before the phosphoric acid is determined, or that the amount of fluoride of calcium must be known and deducted from the pyrophosphate of magnesia. Experiments are now in progress, which have in view the solution of the latter problem, (if possible, in an easy manner); and in the interim, the following process was made use of in those cases where the fluorine was present in such quantities as to interfere with the analysis, and when, as in most cases, the liberated substances were soluble in dilute alcohol. A given quantity of the substance was treated with concentrated sulphuric acid, and evaporated to dryness in a platinum crucible. A few drops of dilute sulphuric and hydrochloric acids were then added, together with a small quantity of water, until the soluble matters were held in solution. Alcohol was then added in proper quantity, and after some time, the whole being thrown upon a filter, the silica and precipitated sulphate of lime were well washed with spirits of wine.

The filtrate after being boiled to separate the alcohol, was mixed with tartaric acid and ammonia in excess, and the phosphoric acid precipitated in the usual manner.

The pyrophosphate precipitates were, under all circumstances, examined for the presence of silica, alumina, and iron, the precipitate being re-dissolved in nitric acid, when if any residuum appreciable by the balance was left, it was weighed and deducted. The filtrate was divided into two portions. One part was boiled with acetate of soda, and if any considerable precipitate was formed, (indicating the presence of iron and alumina), the precipitate was re-dissolved, mixed with the other portion of the filtrate, boiled, tartaric acid and ammonia in excess being added, and the phosphate of magnesia and ammonia re-precipitated and re-weighed. In those cases where no precipitate was produced, or one not appreciable by the balance, ammonia was added in very slight excess, and the precipitate tested

with nitrate of silver for the characteristic yellow colour. If fluoride of calcium had found its way into the pyrophosphate of magnesia, as is always the case in the presence of fluorine, a white precipitate will be formed when the nitric solution is boiled with acetate of soda, even in the absence of anything but a trace of iron and alumina. The white precipitate, under these circumstances, when acted upon with sulphuric acid, etches the glass.

While on the subject of fluorine, it may not be amiss to mention that compounds of this substance may be easily mistaken for other substances, some of which are considered to be most easy of detection.

In a paper, read before the Royal Society of Edinburgh, on the 6th of April, 1846, by George Wilson, Esq., M.D., &c., that gentleman observes, that fluoride of calcium, contrary to all the previous assertions of chemists, is more soluble than fluoride of barium; that an aqueous solution of fluoride of calcium will give a precipitate with salts of barytes, and that this precipitate requires the addition of a large quantity of hydrochloric or nitric acid to dissolve it. He hence infers the difficulty which must arise in distinguishing between the fluorides and sulphates. In June, 1846, I repeated these experiments, and, after many trials, found, that if the fluorides were prepared in silver or platinum vessels, the fluoride of barium, in aqueous solution, gave a precipitate with salts of lime, showing its greater solubility. I then found that ordinary fluor spar, if boiled in glass vessels with hydrochloric acid, would give a precipitate with salts of barytes, and I suspected this to arise from the presence of sulphuric acid. I have since found it to arise from another cause, namely, from the production of fluosilicic acid when fluorides are boiled with acids in glass vessels, or in the presence of silica. If a few grains of any fluoride be boiled with hydrochloric acid, in a test-tube, a solution will be obtained which will immediately give the characteristic reactions of fluosilicic acid, either with salts of potash or barytes. The remarks of Dr. Wilson, as to the difficulties attending the detection of sulphuric acid in the presence of fluorine, are therefore perfectly correct, though they ought to be ascribed to silicofluoric, rather than to hydrofluoric acid."

A geological description of the different strata is then entered into by Mr. Nesbit, and the amount of phosphoric acid contained in these and in the different bodies which they enclose is stated, from which results the following condensed table has been drawn up :

	Phosphoric acid, per cent.
<i>Tertiary deposits.—Crag</i>	0.23 to 0.53
Fossil bones contained in crag (Norfolk)	19.19 , 22.17
Coproliths (Suffolk)	22.30 , 28.74
<i>London clay.—Nodules, probably coprolithic</i>	15.96 , 28.00*
Shark's tooth (Isle of Sheppy)	9.50 —

\* This specimen yielded abundance of fluorine.

<i>Chalk.</i> —Chalk marl (Farnham)	0·79 to 1·99
Upper chalk (Bluebell Hill, Chatham)	0·41 , 0·48
Lower chalk (Thornham Church, near Maidstone)	0·19 , 0·34
Spongite (Black Nez, Calais)	0·29 —
Nodule (St.Catherine's Down, Isle of Wight)	19·00 —
Coprolith	26·92 —
<i>Green marl</i> (Farnham)	2·60 —
Nodules and spongites in green marl	16·47 , 26·56
<i>Green sand</i> (Isle of Wight)	1·23 , 5·48
Various spongites, nodules, casts of ammonites, turrilites, &c., from the green sand	17·23 , 24·26
Nodules from the layer below the above, in the same locality	7·72 , 13·81

*XX. On the Auro-sulphurets of Sodium and Potassium. By COLONEL PHILIP YORKE.*

It was long ago shewn by Stahl, that gold might be obtained in aqueous solution by heating it together with a mixture of alkali and sulphur, and acting on the fused mass by water. Stahl asserts that it was by this means that Moses dissolved the golden calf; and he seems to consider that the nauseous and bitter taste of the liquid, which would render the compulsory drinking of it a fit punishment for the crime of the Israelites, an important argument in favour of this his view.\* But notwithstanding this curious application of his experiment, Stahl's memoir seems generally to have escaped the attention of chemical and other authors,† and no notion of the nature of the combination appears to have been formed until the appearance of the researches of Berzelius on the alkaline sulphurets and the sulphur salts.‡

\* Hoc arte fuisse ipsum illud artificium quo Moses vitulum aureum combusserit, præter facilitatem et simplicitatem negotii, minimum insuper apparatum et quantitatem quoque materiarum exiguum, (siquidem partes 3 salis et partes totidem, aut due solum partes sulphuris ad partem unam auri ita solvendam, imo plus, sufficient) persuadet insuper et illud, quod hoc auratum hepar sulphuris, non modo simul nauseosum illum saporem præ se ferat, quem vulgare et nudum simplex etiam habet, licet re vera hoc minus forteat; sed etiam plane peculiarem penetrantissimam amaritudinem gustui offerat; qualis neque in antimoniali neque alio quoconque hepate deprehendatur.—*Opusculeum Chymico, Physico-medicum*, c. III. p. 607.

† The experiment of Stahl is however quoted by the Abbé Guénée in answer to the objections of Voltaire to the Scripture story.—*Lettres de quelques Juifs*, c. v. et *Petit Commentaire*, 2ème extrait.

‡ De la composition des sulfures alcalins.—*Ann. de Chim.* xx. p. 34, 113. 1822. Mémoire sur les sulfo-sels.—*Ib.* xxxii. p. 60, 166. 1826.

In these memoirs, Berzelius has not only shewn that sulphur is capable of playing the same part as oxygen in the formation of acids and bases, but he has described a great number of sulphur-salts formed by the union of such sulphur compounds, which he had produced and examined. But I do not find in these papers that the sulphur compounds of gold formed the subject of his experiments. In his treatise, indeed, he speaks of a soluble sulfaurate of potassium, but states that it had not been obtained in a solid form, or pure from admixture with liver of sulphur.\*

As my first object was to ascertain the nature of the compound formed in the dry way, after the manner of Stahl, my earliest experiments were made with the view to find the lowest proportions of alkaline base and sulphur, which when heated with gold, would give a compound soluble in water, and also the degree of heat requisite for the purpose. As to the latter, I found that a bright red heat was necessary to obtain any quantity of gold in solution; and from many experiments with different proportions of the substances, it resulted, that when quantities equal to single equivalents of gold, potash, or soda, with three or four of sulphur were employed, about half the gold was dissolved, and that to obtain the whole or nearly the whole in solution, it was best to use a mixture capable of affording two equivalents of the quadrissulphuret of the alkaline base to one of gold.

Thus when	40 grs. of gold, or	1 equivalent
	14 „ carbonate of potash, or	1 „
	14 „ sulphur . . . . .	4-5 „

were put into a porcelain crucible and heated bright red for half an hour, and the fused mass was then digested in water, 19·7 grs. of gold were obtained in solution.

When	50 grs. of gold, or	1 equivalent
	35 „ carbonate of potash . .	2 }
	32 „ sulphur . . . . .	8 }

were used,  $\frac{1}{7}$ ths of the gold was obtained in solution.

Again :	33·3 grs. of gold . . . . .	1 equivalent
	13·3 „ protosulphuret of sodium	2 }
	16·0 „ sulphur . . . . .	6 }

were put into a porcelain crucible and counterpoised, the mixture was fused over a lamp, and then heated bright red in a furnace

\* Traité, vol. III. p. 199, ed. Paris, 1846.

for three quarters of an hour. The crucible, with its contents, had then lost 13·45 grs. =  $\frac{5}{6}$ ths of the weight of the uncombined sulphur; so that there remained only one equivalent of sulphur, beyond that necessary to form protosulphuret of sodium. The gold which remained undissolved when the fused mass was acted on by water, was 2·75 grs.

The solutions obtained in this manner were of a yellow colour, and gave a rich brown precipitate of sulphuret of gold on the addition of any acid.

In order to obtain a crystallized compound, I at first attempted to evaporate these solutions in a retort, but I found that by operating in this way, the solution (of sulphuret of potassium and gold) was decomposed, sulphuretted hydrogen was given off, especially during the early part of the evaporation; a deposit was formed during the whole time, and when the liquid was nearly all evaporated, a colourless saline matter crystallized on the dark precipitate. Water was then added, and the saline solution separated from the precipitate; the solution, on being mixed with hydrochloric acid, gave off the odour of sulphurous acid, and yielded a precipitate of sulphur; when treated with freshly precipitated chloride of silver, the latter was dissolved, and gave a sweet-tasted liquor; the black precipitate proved to be a sulphuret of gold, which, when washed and dried, afforded on ignition 8·1 sulphur for 100 gold; this was therefore the protosulphuret, or Au. S., and the salt formed, was the hyposulphite of potash.\* To avoid the danger of oxidation, I therefore had recourse to filtering the solutions in an atmosphere of nitrogen, in an apparatus contrived for the purpose, and subsequently evaporating in vacuo over sulphuric acid.

*Auro-sulphuret of sodium.*—By experimenting in this manner, and using 100 grs. of gold, mixed with sulphuret of sodium and sulphur in the proportions before stated, I found that when but a small volume of liquid remained, crystallization began, and a crop of well-formed crystals was obtained, weighing about 130 grs. The crystals were of a yellowish colour and prismatic form, but to purify them further from the excess of sulphuret of sodium contained in the mother-liquor, they were re-dissolved and re-crystallized in vacuo; then, when examined before the admission of air, they were perfectly colourless, and very brilliant, but became instantly slightly brown when air was

\* Messrs. Fordos and Gelis found, that when solutions of alkaline sulphurets, containing an excess of sulphur, were boiled, that the water was decomposed, with the production of sulphuretted hydrogen and a hyposulphite of the alkali.—*Ann. de Chim. 3ème Série, xviii. p. 95.*

admitted into the receiver. They were slightly washed, and then dried as much as possible by pressure between filtering paper.

When a portion of the salt thus obtained was heated in a glass tube by a spirit lamp, it first gave off water, and then sulphur. I made four analyses of it by the following methods :

1st. A solution of 12.28 grs. of the salt was mixed with hydrochloric acid, and the liquid filtered from the resulting precipitate of sulphuret of gold. The sulphuret yielded on ignition 7.44 grs. of gold : the filtrate by evaporation and ignition afforded 2.24 grs. chloride of sodium = 0.88 gr. sodium.

2nd. Precipitated metallic copper, which had been ignited in a current of hydrogen, was mixed with 10.385 grs. of the salt, and put into a glass tube, closed at one end, about five inches long, and a quarter of an inch in diameter ; the mixture was covered by more of the powder of copper, and the tube connected with another of the ordinary form for collecting water, charged with asbestos moistened by sulphuric acid. The tube containing the mixture was then heated, beginning with the pure copper ; in this way, the sulphur was retained while the water was driven into the tube intended to collect it. The water thus obtained weighed 2.2 grs. The tube-retort, with its contents, was then placed in a larger tube and digested with nitric acid to acidify the sulphur ; the undissolved gold, after repeated digestion with nitric acid, was washed and ignited : it weighed 6.325 grs. The liquid was diluted, precipitated by nitrate of baryta ; the resulting sulphate, well washed with hot water and then ignited, weighed 8.17 grs. = 1.12 grs. sulphur. The sodium, estimated by the difference, was = 0.74 gr.

3rd. The apparatus used for the third analysis was similar to that used in the last ; but in the place of metallic copper, about 40 grs. of a mixture of two parts of carbonate of baryta and one part of nitre was mixed with 8.84 grs. of the salt. The water obtained, weighed 2.02 grs. The contents of the tube-retort were then acted upon by hydrochloric acid, and the whole dissolved, except the sulphate of barytes, which, when washed and ignited, weighed 6.46 grs. = 0.888 sulphur. The gold was obtained by evaporating the solution, igniting the residue in a porcelain crucible, then acting on the mass with water ; the gold was left, and after being washed with dilute hydrochloric acid and water, it was ignited, and then weighed 5.26 grs. The sodium, estimated by the loss was = 0.67 gr.

4th. 12.825 grs. of the salt were weighed in a glass tube, which was then placed in a glass-stoppered bottle containing strong nitric acid, and digested until no solid matter remained but the gold,

which when washed and ignited, weighed = 7.7 grs. The liquid was precipitated by nitrate of barytes, the resulting sulphate of barytes weighed 9.75 grs. = 1.32 grs. of sulphur. Sulphuric acid was added to the filtrate from the sulphate of barytes, the liquid again filtered from the excess of barytes, the filtrate then evaporated, and the residue ignited in a platinum crucible with a little carbonate of ammonia: 2.93 grs. of dry and neutral sulphate of soda were thus obtained = 0.955 sodium. The water, estimated from the loss, was = 2.85 grs.

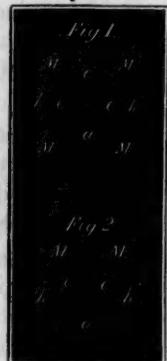
The results of these analyses, calculated for 100 parts, is as follows:

	1st.	2nd.	3rd.	4th.	Mean.
Gold . . .	60.58	60.90	59.50	60.58	60.04
Sodium . . .	7.17	7.13	7.58	7.38	7.31
Sulphur . . .	—	10.79	10.07	10.22	10.36
Water . . .	—	21.18	22.84	21.82	21.94

If we consider the constituents of this salt to be  $\text{Au} + \text{Na} + 2\text{S} + 8\text{HO}$ , we should have for 100 parts,

Gold . . . . .	60.74
Sodium . . . . .	7.10
Sulphur . . . . .	9.89
Water . . . . .	22.26

and we may assume as the rational formula  $\text{NaS} + \text{AuS} + 8\text{HO}$ . The difference between the result of experiment and theory is principally owing to the crystals not being completely purified from the excess of sulphuret of sodium. In an analysis I made before those here given, on a portion of the salt obtained from a first crystallization, this excess was somewhat greater.



The form of the crystals obtained in the first crystallization was a six-sided prism, terminated by a four-sided pyramid, (Fig. 1.) In the second, the form was that given in Fig. 2. The inclination of  $M$  on  $M'$ , as obtained by the reflective goniometer, was  $106^{\circ} 56'$ , of  $M$  on  $k$   $126^{\circ} 4'$ . I could not obtain accurate measurements on the terminal planes.

The crystals speedily became brown and opaque when exposed to the air, and after a time were covered by a brownish efflorescence. The salt was very soluble in water, and was soluble also in

spirits of wine. The addition of an acid to the aqueous solution caused an immediate precipitate of a rich orange-brown colour, with the evolution of the odour of sulphuretted hydrogen, but with very little, if any, effervescence. The quantity of sulphur in the precipitated sulphuret of gold appeared to vary, but was always intermediate between one and two equivalents of sulphur to one of gold.

A solution of sulphate of zinc caused a precipitate of a dirty-orange colour, without any evolution of sulphuretted hydrogen gas; this precipitate, when treated with dilute nitric acid, was partially dissolved, and sulphuret of gold was left.

When the solution was decomposed by the Voltaic battery, the solution being divided into two parts by a porous diaphragm, sulphuret of gold was obtained at the positive pole and metallic gold at the negative;—the quantity of gold eliminated at the positive, being rather greater than that obtained at the negative pole.

When the solution was exposed to the action of the air, it was very slowly decomposed, becoming brown, gradually darker, and at last opaque; it then deposited a black precipitate. The reactions are somewhat complicated, and I have not, as yet, been able to follow them out. The principal resulting bodies appear to be protosulphuret of gold, hyposulphite of soda and caustic soda, or, finally, carbonate of soda.

A solution of gold, formed by dissolving persulphuret of gold in a solution of protosulphuret of potassium, has been proposed by Ruolz \* as fitted for gilding by the electro-process. In order to ascertain the nature of this combination, and the manner of its formation, I began by the examination of the sulphuret of gold which is formed, when a current of sulphuretted hydrogen is passed through a solution of perchloride of gold.

For this purpose I made a solution of gold in aqua regia, in the usual manner, evaporated at 212° F. till the solution crystallized on cooling. The salt was dissolved, the solution filtered, diluted with a large quantity of water, and then precipitated by a current of sulphuretted hydrogen gas, evolved either from sulphuret of strontium or sulphuret of barium and diluted hydrochloric acid. As the moist sulphuret of gold rapidly acidifies when exposed to the air, the sulphuret so obtained was collected on a filter placed in the apparatus before mentioned, filled with nitrogen gas, and there washed; it was then dried in vacuo.

\* Comptes Rendus, 1841, vol. xviii. p. 1003.

The sulphuret of gold obtained in this manner at three different times, was first examined by heating a portion in a glass tube, to ascertain that no water remained, and when found to be anhydrous, the proportion of sulphur was estimated by heating a weighed quantity of it in an open platinum crucible. In this way the quantity of sulphur, combined with 100 parts of gold, was found to be in the sulphuret first prepared 17·2; in the 2nd. 16·1; in the 3rd. 14·93. Of this last, 33·3 grs. were digested for six hours in ether, but when this was drawn off, and the substance dried, it had not lost more than  $\frac{1}{100}$ th of a grain.

The composition of the sulphuret of gold obtained by precipitating perchloride of gold by sulphuretted hydrogen, as given in all chemical works, is 24 parts of sulphur to 100 gold, a result derived mainly from the experiments of Oberkampf;\* and it is considered a tersulphuret; whereas the experiments I have just related would seem rather to indicate that it is a bisulphuret, or 100 gold to 16 sulphur.

But though Oberkampf himself has expressed a doubt as to whether the sulphuret he analysed was perfectly dry, and Javal† has failed, like myself, in obtaining the quantity of sulphur which Oberkampf did, I have found so many discrepancies and difficulties, particularly from the quantity of combining sulphur appearing to be affected by the temperature of the solution of chloride, that I must postpone at present any further discussion of the composition of this sulphuret of gold, and pass on to the consideration of the compound formed by the action of the solution of monosulphuret of sodium on the sulphuret of gold which I had obtained.

For this purpose, I prepared the crystallized hydrate of sulphuret of sodium, and digested in a solution of this substance about 40 grs. of the sulphuret of gold. The clear liquid which was thus obtained was of a golden yellow colour; it was drawn off and evaporated in *vacuo*; it thus afforded a crop of crystals which was nearly colourless, while the mother-liquor was of a deep yellow colour. The crystals were removed, and dried by filtering paper; on examination, they proved to have the same form as the salt already described, individuals being observed resembling Figs. 1 and 2. An approximate measurement by Leeson's microscopic goniometer gave the incidence of  $M$  on  $k = 126^{\circ}$ . On analysis, it became evident that the salt had also the same composition as that previously obtained in the dry way.

\* Ann. de Chim. LXXX. 141.

† Ann. de Chim. XVIII. 343, 2nd Series.

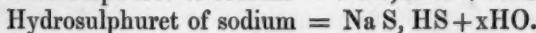
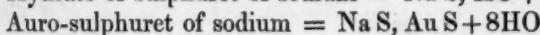
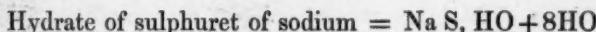
100 parts gave	Gold . . . . .	58·5
	Sodium . . . . .	7·7
	Sulphur . . . . .	10·4
	Water . . . . .	23·3

The solution of these crystals was colourless, and the addition of an acid, caused as before, a dark brown precipitate. The yellow mother-liquor, on the other hand, when similarly treated, gave only a fawn-coloured precipitate, containing but a minute quantity of gold.

What took place in this experiment, therefore, admits of easy explanation. The bisulphuret of gold employed gave up half its sulphur to a portion of the sulphuret of sodium to form bisulphuret of sodium, while the remaining protosulphuret of gold combined with another portion of the monosulphuret of sodium to form the crystallized salt.

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The crystallized hydrate of monosulphuret of sodium, is generally obtained in the form of a square prism, terminated by a four-sided pyramid, and the composition, according to the analyses of Boudet and Kircher,\* is 1 atom of sulphuret of sodium and 9 atoms of water, which agrees with the result of some experiments of my own. So that, although their crystalline forms do not appear to be reconcileable, there exists between this substance and our gold salt, and also the hydrosulphuret of sodium, an analogy of constitution which is worthy of remark, and which may be thus exhibited :



These relations made me desirous to ascertain the quantity of water and the form of the crystals of the hydrosulphuret of sodium ; and I accordingly prepared a specimen of this salt, which crystallized in long four-sided prisms ; but its extreme tendency to deliquesce, made me abandon any further researches upon it.

*Action of hydrosulphuret of sodium (Na S, HS) on sulphuret of gold.*—When the sulphuret of gold was digested in a solution of hydrosulphuret of sodium (Na S, HS) at the temperature of the atmosphere, or a little higher, a slight evolution of gas took place, and but a small quantity of sulphuret of gold was dissolved ; the sulphuretted hydrogen appearing to resist further displacement by

\* Berzelius, *Traité*, vol. II. p. 87, 2nd ed. Paris, 1846. *Rapport annuel*, 1840, p. 45.

the substance. When the solution was boiled, sulphuretted hydrogen gas was given off, but the sulphuret of gold was reduced to the metallic state, and none was dissolved.

*Auro-sulphuret of potassium.*—Quantities of gold, protosulphuret of potassium and sulphur, in the proportions of one equivalent of the first, two of the second, and six of sulphur, were mixed and heated in a porcelain crucible, as in former experiments. The crucible was counterpoised before heating, and weighed again when removed from the furnace and cooled. The fused mass was digested in water; then, calculating the amount of gold in solution by deducting that which remained undissolved, and the amount of sulphur, by deducting the loss suffered by heat, it appeared, that beyond the sulphuret of potassium, one equivalent of gold and one of sulphur were contained in solution. The liquid was filtered and evaporated as before; when but little remained, it had the aspect of a thick syrup; the evaporation was continued to dryness, and there remained a yellow mass, consisting of extremely minute prismatic crystals, which was deliquescent. As there did not appear to be any hope of being able to purify this substance by crystallization, I made no analytical experiments upon it.

After being pressed between the folds of bibulous paper, it gave a colourless solution in water, which behaved like the solution of the auro-sulphuret of sodium.

XXI. *Researches on Coal Tar.* By CHARLES BLACHFORD  
MANSFIELD, B.A.

PART I.

*Introductory remarks.*—The products of the destructive distillation of matters of complex and indeterminate composition are deficient in the interest which attaches to products, the constitutional relations of which to the bodies from whose decomposition they result, may be traced in the phenomena attending the process, or in the nature of the original substances. The absence of retrospective interest is, however, compensated to some extent in the case of pyrogenous products, which are obtained in large quantities from established processes in the arts; firstly, when they are viewed as primitive materials demanding, with the rest of nature, to be interpreted and applied by human industry, (for the artificial is only a particular case of, and nowise distinct from, the natural);

and, secondly, by the prospective interest connected with the distinct substances of much scientific importance, which may be isolated from them in abundance, but which could only be obtained in minute quantities from the sources which afforded them in the first instance. It is remarkable, however, that modern chemistry, with its rapid strides, has left on this extensive field but few foot-prints, whose impressions are distinct and likely to be durable. Although numerous researches, connected with very eminent names, show that the importance of a correct natural history of the substances known as tars, has not escaped the consideration of chemists, yet the meagre and indefinite details on these subjects, which are to be found in our scientific manuals, indicate that much yet remains to be accomplished.

The acid and basic components of the tars (and some of the ingredients of the aqueous parts of the products of distillation), have been more fortunate than their neutral associates in having been submitted to investigation, and designated by names, but there can be little doubt that, even of these, there are others awaiting the friendly hand of the chemist to redeem them from obscurity. Our acquaintance with the constitution of the neutral oils of the various tars has been, with few exceptions, limited to the fact that they are mixtures of various hydrocarbons, of which but few are announced as having been separated, and of these few, a still smaller fraction can claim satisfactory evidence of having been successfully isolated.

The examination of the fluid resulting from the compression of oil-gas\* by Faraday, and that of resin tar by Pelletier and Walter,† are almost the only researches upon the neutral liquid pyrogenous oils, which have yielded exact results; and, in the latter of these instances, the partial nature of the methods employed, render it probable that the subject was far from exhausted, since, for instance, the wholesale and assiduous treatment with concentrated sulphuric acid, to which the products were subjected, would probably exclude from the final results some substances of a neutral nature, which were unable to resist the action of that agent.‡ It is evident, from the unsatisfactory accounts which we receive of the eupion, obtained by Reichenbach from wood tar and from animal tar, that hydrocarbons have been confounded under this one name, which possess properties very different one from another, so that the whole subject, so far as relates to the neutral oils, requires re-examination. The oils

\* Transactions of the Royal Society, 1825.

† Annales de Chimie et de Physique, 1838. T. 67, p. 269. ‡ Vide note, p. 254.

of coal tar have been in the same predicament ; it appears somewhat strange that, in this country, where coal tar is so exceedingly plentiful, that our chemists should have been contented with the discovery of naphthaline, and should have allowed others, less fortunate than ourselves in being able to command abundance of this almost national production, to inform us of the existence at our feet of vast quantities of aniline, of paranaphthaline, and of other remarkable substances ; and it appears, perhaps, no less singular that we should have failed as yet in applying them, when discovered, to the practical uses, which they will, no doubt, some day claim.

These considerations would render it unnecessary that Dr. A. W. Hofmann should back with much persuasion his suggestions to a student to undertake the further examination of coal tar. The researches, a portion of which it is the object of the present paper to communicate, were commenced at the request of Dr. Hofmann, and were conducted, thus far, chiefly in the laboratory of the College of Chemistry, under his valued and friendly advice. It has been, perhaps, the tedium of the methods necessary to effect a separation of mixed hydrocarbons from each other, which has deterred experienced chemists from devoting their time to disentangling the oils here treated of : and, perhaps, to have conducted the innumerable distillations necessary for this purpose in a laboratory imperfectly furnished with gas and other conveniences, would have been a task too laborious to have been persisted in.

It may confer an interest upon the subject of this paper, if what has been hitherto known of the constitution of coal tar, be briefly epitomized ; for the details which we possess on this subject, are scattered few and far-between over the various journals of European science, and the digests of this information to be found in our manuals, are by no means complete or accurate.

*Of coal tar as hitherto described.*—The term coal tar is here, as usually, applied to the black oily matter produced in the distillation of the varieties of bituminous coal, at high red heats, for the production of illuminating gas, as is ordinarily practised in gas-works. The substances which may be obtained by distilling the coal at lower temperatures are not here considered : indeed, but little is known at present of the modifications produced in the distillates, by variations of temperature in the retorts, or of the general relation between the character of the products, and the nature of the coal decomposed.

This coal tar, then, is known to be made up of numerous oily constituents, neutral, acid and basic ; the neutral members of which

assemblage form an overwhelming majority, and have not yet commanded the attention they deserve. It is remarkable, however, that of each of these classes, one representative has taken a leading position in the development of some of the most interesting facts of modern chemistry; than naphthaline, aniline, and phenole, few substances have contributed more by their products of substitution, and by the relations which they exhibit with other bodies, to the extension of the theory of compound radicals.

Among the acids of coal tar may be mentioned acetic acid, some of the acids of the cyanic series, and hydrosulphuric acid; but these belong rather to the aqueous liquor, than to the oily part, of the distillate. Of the acid oils we know but little. Runge\* described three, which he denominated carbolic, rosolic, and brunolic acids. Of rosolic and brunolic acids we have heard no more since Runge spoke of them, and their existence must be considered doubtful. The presence, however, of carbolic acid in the tar has been confirmed by Laurent,† who has analysed and described it under the name of hydrated oxide of phenyle (phenole,  $C_{12} H_8 O$ , HO). It is probable also that, unless the creosote, which Reichenbach‡ prepared from wood tar, be the same substance in an impure state, that creosote also is present.

Of basic substances, ammonia abounds, and Runge§ introduced three others into notice: pyrrol, kyanol (aniline  $C_{12} H_7 N$ ) and leukol (leukoline,  $C_{18} H_8 N$ ), the two last of which Dr. Hofmann|| has placed, by his analyses, on the list of chemical realities. Of pyrrol nothing is known except that, according to Runge's account of it, it is a gaseous substance, that exists in very minute quantities in the oil of coal tar, as well as in animal tar. From Runge's description, the basic quality, which he assigns to it, seems rather doubtful; however, it is certain that the crude oil, especially the more volatile portion of it, does give the red colour to pine-wood dipped in hydrochloric acid, which Runge mentions as characteristic of pyrrol, and that it loses this property after agitation with a sufficient quantity of dilute acid. More recently, Dr. Anderson,¶ of Edinburgh, has isolated and analysed the remarkable base, picoline, ( $C_{12} H_7 N$ , isomeric with aniline), whose peculiar odour prevails in the more volatile coal-oils.

\* Poggendorf's Annalen, Bd. 31, s. 65, 513, and Bd. 32, s. 308, 328.

† Annales de Chimie et de Physique, Sér. 3, t. 3, p. 196.

‡ Schweigger Seidel's Journal, Bd. 65, s. 461.

§ Pogg. Annal. loc. sup. cit.

|| Annalen der Pharmacie, Bd. 47, s. 37, and Philosophical Magazine, 1844, March and April.

¶ Edinburgh New Philosophical Journal, 1846, July.

Of neutral substances, the solid hydrocarbon naphthaline ( $C_{20} H_8$ ) is universally known, and is remarkable as existing in such enormous quantities in some samples of tar, as to form nearly a quarter of the whole mass; while in others there is so little of it, that to obtain it at all is a matter of some difficulty.\* Paranaphthaline ( $C_{30} H_{12}$ ?) another beautiful solid, vastly abundant too, is less known, having been discovered by Dumas,† and subsequently treated of by Laurent‡ under the name of anthracène. This substance is, perhaps, identical with the metanaphthaline, which Pelletier and Walter§ obtained from resin tar, and which it resembles in composition, as well as in many of its properties, though the latter authors were inclined to believe them different. Chrysène ( $C_{12} H_4$ ?) and pyrène ( $C_{15} H_6$ ?) are other solid hydrocarbons referred by Laurent|| to coal tar, but of whose exact character some doubt is still entertained.¶ The

\* There probably was but little naphthaline in the tars from which it was originally obtained, for Kidd, who first described a method of preparing it from coal tar (*Philosophical Transactions*, 1821, p. 209), conceived it necessary to pass the tar vapours through a red hot tube. Indeed, ten years after its discovery, it was still a matter of speculation whether naphthaline existed in coal tar, or was a product of its decomposition, till Laurent (*Annalen der Pharmacie*, Bd. 3, p. 9, 1832) decided the question. But even then it was considered necessary to expose the tar to freezing mixtures, or to the action of chlorine gas, in order to make it yield up its naphthaline. It is probable that the tar of the London gas-works at present contains more naphthaline than that of former days. It may be useful to state that this interesting substance may be procured in enormous quantities at many of the tar-works, where it is deposited, mixed with para-naphthaline, by the oils distilled from the tar, in granular crystalline masses, called "salts," by the workmen. It is there thrown away as useless, or, at best, burned for lamp-black; and yet it is honoured in our chemical catalogues with a price of four or five shillings per ounce. In the tar of Scotland and the north of England, where cannel coal is much used, naphthaline is still a scarce article.

† *Annales de Chimie, &c.*, t. 50, p. 182.

‡ *Annales de Chim.*, t. 60, p. 220; t. 66, p. 149; and t. 72, p. 415.

§ *Ann. de Chim.*, t. 67, p. 269. || *Ann. de Chim. F.* 66, p. 136, 146.

¶ Laurent omitted to prove the existence of chrysène and pyrène in coal tar. He has described and analysed two substances, which he separated from the orange-coloured matter appearing among the last products, volatilized at a high temperature, from a sample of oil tar, (*Ann. de Chim.*, t. 66, p. 136). He assumed the identity of this product with the similar substance obtained from coal tar in the last period of distillation. This "yellow farina," as it is called by Kidd, appears to have been first noticed by that chemist, in his experiments on coal-tar, which are recorded in his paper on naphthaline, (*Phil. Trans.*, 1821, pp. 212, 219). The last volatile products of the destructive distillation of a variety of organic matters present the same appearance, (see Bussy and Lecanu, on the "Distillation of fixed Oils," *Ann. de Chim.*, t. 30, p. 1, and other authors referred to by Laurent in the paper above cited), which has been aptly compared to that of realgar; but the identity of all these matters, though probable, requires demonstration. This substance has now been obtained in large quantities in a process of distillation of coal pitch, recently introduced by Mr. John Bethell, who has kindly supplied some of it, as well as of the other products of the tar, for an examination to which it is intended to submit this series of empyreumata, and which will form a subject for a future communication.

three last are among the least volatile part of the tar, and are probably the chief constituents of coal pitch, occupying the position which paraffine partly fills in wood pitch; they can be distilled only at temperatures above 300° C. (572° F.)

Of the liquid neutral oils of coal tar, which generally constitute about half the bulk of the tar, we have no precise information; and the present paper is intended as a contribution towards the filling of this hiatus.

The terms coal-naphtha,\* and oil of tar, have generally been used in chemical works in a very indefinite manner, apparently from the want of precise notions of the nature of, and mode of procuring, these fluids. A short account, therefore, of the usual mode of treating the tar, and of the general nature of the products, may render more perspicuous the subsequent details.

*Of the products usually obtained from coal tar.*—Coal tar† is a black, thick, oily substance, insoluble in, and heavier than water, a considerable quantity of which, however, the tar usually retains in mixture. The distillation of coal tar is a regular branch of trade, and the operation is usually conducted in large iron retorts capable of holding many hundred gallons. The first products that come over are ammonia, and probably other permanent gases; as the temperature rises, water charged with various ammoniacal compounds passes over, accompanied by a fetid yellow or brown oil, which floats on the water in the receiver. This oily distillate gradually increases in quantity and density, and the water appears in smaller proportion; after some time, the oil distils over of such density, that

\* The very loose application of the name "naphtha," which originally belonged to volatile hydrocarbonaceous liquids found at certain places in the earth, and which has since been adopted for the somewhat similar substance distilled from coal tar, as well as for the very different pyroxylic spirit, is productive of frequent inconvenience. A greater precision in our common nomenclature is highly desirable. It would be an improvement, perhaps, if the word "naphtha" were accepted as a generic term for liquid hydrocarbons of ascertained or probable pyrogenous origin, (or even without this restriction), and if a special prefix were always used to indicate the nature of every particular instance. Thus earth or native naphtha, schist naphtha, animal naphtha, &c., would be at once intelligible. Wood naphtha would designate the interesting hydrocarbonaceous fluids of wood tar, and would leave the term "wood spirit" to the compound to which it is already appropriated, and which has already as many synonyms as can reasonably be required. Additional epithets would mark the distinct substances obtained from any one source: thus, in the case of coal tar, which yields two sorts of oil having the well-marked difference of being, one lighter, the other heavier than water, there would be light coal naphtha, and heavy coal naphtha, which terms will be adopted in this paper.

† The specific gravity of coal tar varies from about 1·120 to 1·150; the lightest samples containing the largest proportion of fluid oils. It exceeds most other tarry

it sinks in water; the receiver is now usually changed, and the previous oily distillate set aside as "light oil," or "crude naphtha." The tar generally yields from 5 to 10 per cent of the "light oil," which will here be termed "light coal naphtha," or, for brevity, "light naphtha," when "coal" will be understood to be implied. As distillation proceeds, heavy oil continues to run, free from water, very fetid, and of a yellow colour. If much naphthaline is present in the tar, a large proportion of the earlier part of the heavy oil solidifies on cooling; frequently, however, the distillate shews no signs of solidification till a quantity of heavy oil, equal to about 30 per cent of the tar, has come over; distillation always begins to flag at this stage, and the operation is usually stopped. The black residue which remains in the retort, and which solidifies into a hard vitreous mass on cooling, is "pitch," and is applied to the purposes of making asphalte &c., or, when dissolved in a part of the fluid oily distillate, to the production of a black varnish much used for iron-work. The heavy oil, whose extrication forms the second period of the process, is technically called "dead oil," and will be referred to below as "heavy coal naphtha," or "heavy naphtha."

If the distillation is to be carried farther, a much higher temperature is required, and it is necessary to run off the pitch into smaller retorts. The product next obtained is, when cool, a greasy substance, of the consistence of butter, which is chiefly paranaphthaline; as the operation proceeds, the texture of the distillate becomes more resinous, and its colour yellowish. Finally, when the heat of the retort approaches redness, the vapours which escape from

matters in density. The tar obtained in the distillation of beech, or oak wood, has a sp. gr. about 1·110. The tar from resinous trees is usually still lighter, Stockholm tar standing at about 1·040. A species of native tar, or petroleum, recently described by Dr. Ure (*Pharmaceutical Journal*, vol. 7, p. 485) as issuing from the earth in Derbyshire, is remarkably lighter than any of these, being of no greater sp. gr. than 0·900. Since the production of tar naphtha from coal by distillation, it has been a frequent and natural inference, that some of the many instances, in which petroleum and earth naphtha occur, were the results of destructive distillation going on in coal strata subjected to volcanic heat; and some authors have ventured to assert the identity of the artificial with the native product. The appearance in a coal mine (near Alfreton) of the substance just mentioned, rendered the question of its similarity to coal tar extremely interesting. The kindness of Dr. Ure, in offering a sample for examination, gave the opportunity of comparison. The native tar was found to consist chiefly of fluid oils, boiling at temperatures above 300° C. (572° F.), containing scarcely any solid matter, and a very small quantity of oil boiling below 200° C. (392° F.). The physical characters exhibited by a cursory examination were thus quite sufficient to mark the substance as in every way distinct from ordinary coal tar. Its odour is entirely different from that of coal tar, or of any of its constituents, bearing, however, some resemblance to that of the oil distilled from bituminous schist.

it condense in the form of a bright, orange-coloured powder, which is free from odour, and which, when pressed between the fingers, agglutinates into a viscous mass.\* The residue now left in the retort is a beautiful coke, of a more or less porous structure, of extreme hardness, and difficult of combustion.

The heavy coal naphtha is seldom rectified; it is used chiefly for burning into lampblack, for coarse lamps or torches, and for the preservation of timber by impregnating it with the oil. Its antiseptic properties are remarkable, and may be owing partly to the hydrocarbons of which it chiefly consists, and partly to the carbolic acid, or to the creosote which it contains—(this, however, is not stated as affording any explanation of the fact). It contains aniline and leukoline, and probably other basic substances less volatile than these, which are yet to be discovered.

The crude light coal naphtha is rectified, either by distilling it from retorts, heated in the usual manner, or by driving steam through it; in either case, a further portion of heavy naphtha is separated from it as residue. The light naphtha thus rectified, has still a disagreeable smell, and, though colourless at first, gradually acquires a brown colour when kept, by the conversion of one or more of its components into non-volatile resinous matter. This coloration is usually, and with correctness, probably, assumed to be a result of oxidation. The light naphtha is further purified for commerce by treatment with some substance which removes the bad odour, to a greater or lesser extent, and completes at once the conversion of the colouring matter. The agent usually applied is oil of vitriol, which, on agitation with the distillate, acquires a deep red colour, with which it leaves the supernatant fluid more or less tinged. After another distillation, the oil should now be permanently colourless, free from naphthaline, and without offensive odour. It is evident, however, that by such treatment, some neutral substances, besides naphthaline, which, like that body, may have an attachment to sulphuric acid, may be removed, and would, therefore, be missed in an examination of the purified material of commerce.

*Of the product first examined.*—The subject of the first part of the present investigation, was the crude light coal naphtha, as obtained from the tar distiller. Many samples of this product, from works in various parts of England, have been examined; and it is remarkable that the general constitution of all has been found to be the same;†

\* Vide supra, p. 248.

† There is much greater difference in the qualities of the "rectified naphtha," which depends upon the stage of the rectification at which the receiver was removed, and on the

the only manifest difference being in the quantity of naphthaline present, which, as before stated, varies greatly in different samples. This crude naptha is a yellow or brown mobile fluid of, sp. gr. about 0·900 or 0·950,\* rather redolent of ammonia, of picoline, and of other unpleasant bodies.

If distilled, it begins to boil generally about 100° C. (212° F.) ; and, as this continues, the temperature rises steadily up to about 200° or 220° (392°, 428° F.) The last portions of the distillate solidify on cooling, if much naphthaline be present (as is generally the case in naptha made from London tar) ; and the residue in the retort is a dark brown resinous substance, resembling pitch. This, however, is not the same substance as the pitch residue of the tar above mentioned, but consists chiefly of the matter formed by the oxidation of some of the volatile fluids in the naptha ; so that, if the heat be urged farther, decomposition takes place, a red oil distils over, having a smell entirely different from that of any of the tar oils, accompanied by a small quantity of water which is formed in the retort, but little or no paranaphthaline appears.

*Of the examination of the light coal naphtha.*—The method, which was actually adopted in the laboratory, for the separation of the substances in the *coal-oil*, will be first described, as it is, perhaps, the only method which promises much security for the detection of all the fluids present in such mixtures. It is in principle the same as that which Faraday applied to the dissection of the *oil-oil*. The details here given will render unnecessary many repetitions, which would otherwise be requisite in future communications, in which it is intended to relate the results of an investigation of the other tar products. Subsequently, more compendious methods will be pointed out, by which some of the bodies, once detected,

consequent exclusion or admission of the less volatile of the fluids, which will be described below : the quantity of sulphuric acid, or other decomposing agents, which have been used in the deodorizing process, of course also materially affects the character of the produce.

\* The specific gravity of the product sold as "highly rectified," varies from about 0·860 to 0·900. The indications of the hydrometer are, to a certain extent, indicative of its purity, but they are very vainly, as well as universally, imagined by the distillers of coal naptha to be as truly a criterion of the "*strength*" of their samples, as it is of the quantity of alcohol in spirit. What notion they attach to "*strength*," as regards a fluid not capable of dilution with water, is not very apparent. If they mean volatility, their test is erroneous, for all the hydrocarbons, except naphthaline, which the pure "*light oil*" ever contains, are nearly of the same specific gravity, the most volatile of all however, being the heaviest, *i. e.* about sp. gr. 0·870; so long as the density of the liquid is greater than this, its sp. gr. will be an index of *purity* (*i. e.* of its freedom from naphthaline, and from hydrocarbons having higher boiling points than that body, and from acid and basic oils, all of which increase its specific gravity, and, for the most part, diminish its volatility) but beyond this, the comparison is fallacious.

may afterwards be practically prepared for experiment. The object of this investigation being the neutral oils, the first step was to obtain them free from basic and acid substances. For this purpose, two gallons of the crude light coal naphtha were agitated frequently with a gallon of a cold mixture, of about nine parts of water, with one of sulphuric acid, which was so far diluted to destroy any tendency it might possess to decompose, or to form compounds with, the hydrocarbons. After the separation of the fluids, the oil was drawn off from the acid, and washed with water. It was then similarly treated with a dilute solution of potash, and again washed. This treatment with acid and alkali having been repeated, the oil had now lost much of its bad smell; an improvement in this respect having followed the application of each of these agents.\*

The light naphtha thus purified, was distilled in convenient quantities of about a quart at a time in glass retorts, a thermometer being kept immersed in the fluid, and regular ebullition being constantly maintained. The boiling commenced at about  $100^{\circ}$  ( $212^{\circ}$  F.) The thermometer continuing to rise constantly as the distillation proceeded; when the temperature had reached  $150^{\circ}$  ( $302^{\circ}$  F.), about two-thirds of the contents of the retorts had distilled over, the greater portion of the remainder coming over below  $200^{\circ}$  ( $392^{\circ}$  F.). When the mercury stood at a little above  $200^{\circ}$  ( $392^{\circ}$  F.), the distillate began to solidify on cooling, and was now heavier than water. Attention is for the present restricted to the fluids received previously to the appearance of solid matter in the condenser. From similar results obtained from other samples, it was evident that, what is usually called "coal naphtha," consists chiefly of a mixture of oils having boiling points below  $200^{\circ}$  ( $392^{\circ}$  F.)† (and, consequently, more volatile than naphthaline, which boils at  $212^{\circ}$ ) ( $414^{\circ}$  F.); so that the subject of present inquiry is conveniently defined. The distillates were mostly colourless, or nearly so, a pale yellow appearing in the latter portions, the brown colouring matter remaining concentrated in the residue. During the distillation, the receivers were changed at regular intervals of five degrees ( $9^{\circ}$  F.) of increasing temperature.

\* Before treatment with acid, the light oil would tinge a piece of white deal yellow, or, if the wood had been previously dipped in hydrochloric acid, purplish red. The first of these reactions was probably due to some salts of aniline; the second, perhaps, to the substance indicated by Runge as pyrrol. It had also the power of destroying the texture of the human cuticle, which Reichenbach mentions as belonging to creosote (*Annalen der Pharmacie*, Bd. 4, s. 275), and which is possessed more strongly by the crude heavy coal naphtha; so that the skin of the hands, after being touched with it, becomes dry and scales off. These properties had disappeared from the purified oil, which had, however, but little diminished in bulk.

† The heavy coal naphtha consists chiefly of hydrocarbons, boiling between  $200^{\circ}$  and  $300^{\circ}$  ( $392^{\circ}$ — $572^{\circ}$  F.), with more or less of paranaphthaline in solution.

A series of products were thus obtained, consisting of mixtures gradually decreasing in volatility. These were then submitted to a second distillation, in turn, commencing with the first received; the vessels were again changed at every 5th degree of heat (9° F.) in the retorts. A great depression was now observed in the point at which ebullition commenced in the case of each successive fraction, while, on the other hand, the thermometer index rose far higher than the superior limit of temperature, below which the same fluid was distilled in the previous treatment: for instance, the fraction, which commenced from the boiling point 110° (230° F.) in the first order of operations, began to boil at about 90° (196° F.) in the second; while of the same portion, all of which was received below 115° (239° F.) in the first, more than a quarter remained unvolatilized at 120° (248° F.) in the second ebullition.\* So that each fraction of 5° (9° F.) was distributed over 30° or 40° (54° or 72° F.) of the scale in the second order of receivers, in which the fractions corresponding to the same temperature from each successive retort of the second series, were mixed together, and kept separate from the others.

Thus a second series of distillates is presented; for each 5° (9° F.), from 90° to 200° (196° to 392° F.). In the same manner this series is again dispersed over the range of boiling heats, by a third succession of distillations, and again collected in a separate set of receivers. The depression of the first boiling point is now lessened, and the extent of scale traversed by the thermometer is more contracted in each separate retort, than in the preceding series. An approach towards purity, or, at least, towards an inferior degree of complexity is thus attained in each fraction. New series of distillations, conducted in the same manner, give successive advances in the desired direction.

Of the first order, all the fractions were almost exactly of the same bulk, especially between 100° and 170° (212° and 338° F.) In each later series, however, a greater quantity distilled over at certain temperatures than at others, so that the points of most copious produce converged towards certain centres of temperature, indicating clearly that, in

\* This inevitable result of the distillation of a medley of fluids in solution in each other, has, in some cases in which it has been observed, given rise to the notion, that, on each ebullition, a fluid, which has been assumed to be a definite compound, has been decomposed into other products, some more, some less volatile than the original substance. (Vide Pelletier and Walter, Ann. de Chim., t. 67, p. 269, on Retinole, where it will be seen that their observations on this subject throw doubt on their analysis of their supposed pure hydrocarbon.) During all the distillations, to which the coal-oils have been submitted in the present treatment, nothing has appeared that could cause the slightest suspicion, that they, at their boiling temperature, under ordinary pressures, have ever the faculty, like amputated earthworms, of growing into separate bodies, or, like star-fish vexed, of casting off their offending members in spasmodic suicide.

the naphtha, the quantity of fluids, having boiling points near such temperatures, was much greater than that of fluids having intermediate stations.

*Of the results of the examination.*—Thus, after ten distillations of the whole quantity, a series of fluids were obtained, having boiling temperatures between 60° and 190° (140° and 376° F.) ; and of these, the *maxima* were between 60° and 70° (140° and 158° F.), between 80° and 85° (176° and 185° F.), between 110° and 115° (230° and 239° F.), between 140° and 145° (284° and 293° F.), and between 170° and 175° (338° and 347° F.) So that the fractions corresponding to some of these temperatures, were about three times as great as some of the others. The boiling *spaces*, within which any one of these would now distil, were very much contracted, but not yet reduced to *points*; more than half of each quantity coming over within the limits of its previous ebullition,—thus, of 15 ozs. received from the ninth series of retorts between 110° and 115° (230° and 239° F.), nearly 8 ozs. distilled between the same limits on the tenth rectification, ebullition commencing at 106° (223° F.), and not  $\frac{1}{2}$  oz. remaining in the retort at 120° (248° F.) The operation was always stopped when the distillate, from the less volatile oils, began to solidify in the condenser, so that, from the last fractions of each series, a quantity of naphthaline, less on each successive rectification, was eliminated, till it finally disappeared from all the fluids obtained at temperatures below 190° (376° F.).

In the earlier distillations the retort-contents acquired, as ebullition continued, a pale brown colour, especially in the fractions between 130° and 160° (266° and 320° F.), and the colouring matter remained in the retorts as residue. The more volatile liquids left no residue in the later distillations. All the products were colourless; but those, even of the tenth order, that came over about 140° (284° F.), after being kept some time in glass bottles, became slightly coloured, and deposited a brown film on the glass, though the others remained clear as water. The specific gravities of all the fluids were nearly the same, when the less volatile were quite free from naphthaline; all having a sp. gr. between 0·86 and 0·88. The most volatile of all having, however, the greatest density. Those which are marked by preponderance in quantity over the others have peculiar odours, by which they may be at once distinguished from each other by a person accustomed to them, though, to an indifferent observer, they all smell alike—of “naphtha.” These odours merge gradually into each other in the intermediate fractions; those of the more volatile oils are the most powerful, and of an ethereal character; those less easily vapourised being rather aromatic. The most volatile

of all the products differs, however, remarkably in this respect from the rest. The maxima about  $70^{\circ}$  and  $170^{\circ}$  ( $158^{\circ}$  and  $376^{\circ}$  F.), were not nearly so great as those about  $85^{\circ}$ ,  $115^{\circ}$ , and  $140^{\circ}$  ( $185^{\circ}$ ,  $239^{\circ}$ , and  $284^{\circ}$  F.); that belonging to  $170^{\circ}$  ( $376^{\circ}$  F.) being deficient, because the greater part of the oil which it represents remains mixed with the heavy naphtha, by which it is kept back on the distillation of the tar.

There is no doubt, then, that at least five distinct fluids enter into the constitution of the light coal naphtha; and it is possible that others will yet have to be added to the list. Each of these substances demands separate consideration.

*Of the oil boiling about  $60^{\circ}$ - $70^{\circ}$  ( $140^{\circ}$ - $158^{\circ}$  F.).*—This liquid is characterized by a peculiar alliaceous odour, somewhat resembling that of bisulphide of carbon, entirely different from that of all the other substances in the naphtha. It is so extremely volatile, that it is probable that on each distillation a portion of it escaped condensation; this, indeed, appeared to be the case.\* So small a quantity of it exists in the naphtha, that not more than an ounce was obtained from the two gallons of the crude material used in the investigation. Its examination is therefore deferred for the present, till a sufficient quantity has been prepared by the treatment of a large supply of the most volatile part of the crude distillate from the tar. It is by no means certain that it consists of only a single very volatile fluid, mixed with a certain quantity of the oil received at about  $80^{\circ}$ - $85^{\circ}$  ( $176^{\circ}$ - $185^{\circ}$  F.). It may be mentioned, however, that the greater part of it forms a compound with

\* It has been remarked above, that coal tar probably contains permanent gases (besides ammonia) in solution. It seems not unlikely that the same is true of the more volatile hydrocarbonaceous liquids distilled from it, even after several rectifications; for the fluid in condensing would, of necessity, carry down with it a certain quantity of such gases as were mixed with its vapour, and are copiously soluble in the fluid, while, at the same time, a certain quantity of the vapour of the liquid would escape in solution in the liberated gas. This reflection, supported by Faraday's experiments on the fluids compressed from oil gas (Philosophical Transactions, 1825, and by those of Couerbe on the similar products obtained from resin gas, (Comptes Rendus, v. 7, p. 497), provokes the conjecture that an investigation undertaken with coal gas, by submitting it to powerful condensation, (especially when taken fresh from the hydraulic mains or from the cooling apparatus, and before it has undergone any purifying process), would be rewarded by the detection of some hydrocarbons not hitherto observed:—bodies whose physical state at ordinary temperatures may lie on the verge between the liquid and the gaseous, and whose chemical nature may fill the gap between the simple constitution of marsh gas, or olefiant gas, and the far more complex arrangement of the simplest known hydrocarbon of the tar liquids, the density of whose vapour is to that of olefiant gas as 2.78 to 1, and to that of marsh gas as 4.87 to 1, while its boiling point lies perhaps  $200^{\circ}$  ( $392^{\circ}$  F.) above that at which either of these latter liquefies. (Sp. gr. of benzole vapour, 2.770; of olefiant gas, 0.985; of marsh gas, 0.559.)

oil of vitriol, from which water precipitates a solid substance, having an aromatic odour.

Attention was accordingly turned to the most volatile product that appeared in quantity sufficiently large to encourage examination.

*Of the oil boiling about 80°-85° (176°-185° F.).*—The comparatively slow rise of the temperature, in the retorts, between 80° and 90° (176° and 194° F.), even in the fourth series of distillations, indicated that the fluids received between those limits was of far simpler constitution than at first, and that a considerable quantity of some compound was present, whose boiling point was in this immediate neighbourhood.

Mr. Faraday long ago suspected the presence in coal tar of the "bicarburetted hydrogen," which he discovered in the oil gas liquor; he mentions, however,\* that his search for that substance in coal tar was unsuccessful. Some samples of coal tar contain a very much smaller proportion of the more volatile liquids than others; so that the unfortunate escape of this substance, from the acumen which then threatened its detection, was probably owing to the inquiry having fallen upon unfavourable specimens. However, the subsequent production of the same oil, by Mitscherlich,† from benzoic acid, from which it has derived its present patronymic (benzole), having exhibited the true nature of its constitution ( $C_{12} H_6$ ), and the development of organic chemistry having farther revealed its properties, after twenty years another scrutiny was not to be evaded. Thus Dr. A. W. Hofmann‡ was enabled to shew the existence of benzole in coal naphtha, by means of the test for its presence, which he deduced from its convertibility into aniline. He did not, however, at that time attempt to separate this hydrocarbon from its associate tar-oils.

The observations of Faraday and of Mitscherlich had informed us that this compound boiled at 85°.5, or 86° (186° or 187° F.), and that, like water, it solidified at 0° (32° F.) From these facts, and from the habitudes of the light coal naphtha above described, it was clear that the benzole was to be looked for among the more volatile of the fractions obtained.

*Of the preparation of benzole from coal naphtha.*—The fifth series of the distillations, just spoken of, yielded about a pint of fluid, which had boiled between 80° and 90° (176°-194° F.) It was clear and colourless, of a powerful spirituous odour, in which a refined sense would recognise the fragrance of benzole, though a vulgar organ might be reminded of coal gas.

\* Philosophical Transactions, 1825, vol. 115, p. 465.

† Annalen der Pharmacie, 1844-5, Bd. 55, s. 200.

‡ Annalen der Pharmacie, 1834, Bd. 9, s. 43.

A small quantity of the fluid received on the fifth distillation between  $85^{\circ}$  and  $90^{\circ}$  ( $185^{\circ}$  and  $194^{\circ}$  F.), being exposed to cold, at about five degrees below  $0^{\circ}$  ( $32^{\circ}$  F.), in a test-tube, soon became in part solid and crystalline. The fraction received between  $80^{\circ}$  and  $85^{\circ}$  ( $176^{\circ}$  and  $185$  F.) behaved similarly, while specimens corresponding to temperatures below  $80^{\circ}$  ( $176^{\circ}$  F.) and above  $90^{\circ}$  ( $194^{\circ}$  F.), shewed no signs of solidification, except such of the least volatile as contained naphthaline, which they partially deposited. On being submitted, in a freezing mixture, to a temperature of— $20^{\circ}$  ( $4^{\circ}$  F.) the sample representing the boiling *line*  $75^{\circ}$ - $80^{\circ}$  ( $167^{\circ}$ - $176^{\circ}$  F.) yielded a portion of crystalline matter, and those from  $80^{\circ}$ - $90^{\circ}$  ( $176^{\circ}$ - $194^{\circ}$  F.) became almost entirely solid, while those from  $90^{\circ}$ - $95^{\circ}$  ( $194^{\circ}$ - $203^{\circ}$  F.), and upwards, still suffered not the slightest change of state.

It was now almost certain that benzole was secured, and that the solidification was due to that substance. It was evident, however, that the crystalline product thus obtained would be a mixture of the desired matter with substances having boiling points more or less near to that of the hydrocarbon, in which they were present as impurities; and, that, unless these fluids had the same freezing point as benzole, or would form compounds with it which are solid at the same temperature, they might be separated from it by pressure and filtration. The whole of those fractions of the fifth order of distillates, which had been received between  $80^{\circ}$  and  $90^{\circ}$  ( $176^{\circ}$ - $184^{\circ}$  F.), were treated accordingly.

A very simple apparatus—one of Beart's coffee-pots—effected the purpose. This machine consists of a hollow cylindrical vessel, into which a perforated piston fits tightly, supporting a piece of strong cloth, so as to form an apparatus, in which rapid filtration is effected by the atmospheric pressure, when the piston is forcibly raised through the fluid. The application is obvious. The filter-piston is placed at the bottom of the vessel, which is immersed in a mixture of snow and salt. The fluid to be purified is now poured into the pot, or, better still, is first exposed, in large test-tubes, to the freezing mixture, and from them, when solidified, is transferred to the filter. The crystalline mass may be expelled from the tubes very readily, by holding their mouths downwards, and slightly warming their sides and closed ends with the hand, when a minute quantity, becoming vapourized, will expand, and will force out the solid in the form of mould candles of benzole. The temperature is kept at about  $10^{\circ}$  or  $12^{\circ}$  below  $0^{\circ}$  ( $14^{\circ}$ - $11^{\circ}$  F.) in the filtering vessel, while its contents are stirred and broken down, to prevent passages being left for the air through the mass when the piston is raised, it being essential that the pressure of the substance against the filter should be as great as can be ensured.

When the piston is drawn up, a crystalline mass, like snow in whiteness and texture, is separated from the fluid oil which has passed through the filter. This product is placed in a funnel, the bulb of a thermometer being buried in it, and the temperature is allowed to rise slowly while the thawing fluid is received below. The melting proceeds rapidly at first; more slowly as the temperature approaches  $0^{\circ}$  ( $32^{\circ}$  F.), which point it will pass before the whole has fused. The receivers are changed at intervals of increasing temperature, and their contents, being separately subjected to another refrigeration, and again liquefied in like manner, yield further portions which remain solid above  $0^{\circ}$  ( $32^{\circ}$  F.). These last, together with that which in the first instance was still congealed at  $0^{\circ}$  ( $32^{\circ}$  F.), prove to be nearly pure benzole. It is usually found that the thermometer indicates  $4^{\circ}$  or  $5^{\circ}$  above  $0^{\circ}$  ( $39^{\circ}$ - $41^{\circ}$  F.) before all the substance in contact with its bulb is fused. The portion that quits the solid state last, is found to be a fluid which crystallizes now at a temperature a little above  $0^{\circ}$  ( $32^{\circ}$  F.), and boils *constantly* at  $80^{\circ}$  ( $175^{\circ}$  F.) in glass vessels with pieces of platinum wire at the bottom, distilling over without leaving a trace of residue in the retort. It is, therefore, a pure substance.

It remains to confirm the identity of this substance with benzole, which its properties so strongly indicate.

This fact is supplied by an analysis, which was made by Mr. E. C. Nicholson, of the fluid thus prepared, the results of which were:

	Grammes.
Substance burned with oxide of copper . . .	0.2028
Results of combustion { $\begin{matrix} \text{CO}_2 & : & : & : & : \\ \text{HO} & : & : & : & : \end{matrix}$	$\begin{matrix} 0.6840 \\ 0.1405 \end{matrix}$
<i>i. e. per cent.</i> { $\begin{matrix} \text{C} & : & : & : & : \\ \text{H} & : & : & : & : \end{matrix}$	$\begin{matrix} 91.98 \\ 7.69 \end{matrix}$

The per centage of the elements of benzole, as calculated from its admitted formula  $\text{C}_{12}\text{H}_6$ , being

C . . . . .	92.3
H . . . . .	7.7
100.0	

By subsequent rectifications of the naphthas, whose boiling *lines* in the fifth series of distillations had extended some distance above  $90^{\circ}$  ( $194^{\circ}$  F.), a further produce of fluid crystallizable by the above process was obtained, so that the two gallons of light coal naphtha yielded about a pint of nearly pure benzole.

*Of some of the physical characters of benzole.*—The fluid thus isolated, though readily crystallizable at  $0^{\circ}$  ( $32^{\circ}$  F.), may be cooled to a temperature considerably lower, in a smooth glass vessel, kept still, without change of state; but if, when in this condition, it is agitated, especially if poured into another vessel, it will instantly congeal. When rapidly solidified, it presents the appearance of a crystalline white wax, or of camphor, like which substance it will take fire at a flame, and will burn without immediately fusing. When cooled very slowly, it crystallizes in beautiful cruciform leaflets, of perfect transparency, which aggregate into forms resembling fern-fronds, with numerous pinnæ at right angles to a principal axis.

Repeated experiments have shown that it boils, at ordinary pressures, at a temperature a little above  $80^{\circ}$  ( $176^{\circ}$  F.), but not higher than  $81^{\circ}$  ( $178^{\circ}$  F.);\* and it is worthy of remark, that a sample of benzole, prepared from benzoic acid by Dr. Hofmann, observed by the same thermometers, in glass vessels containing metallic fragments, boils at the same point. The observation of Mitscherlich† had placed the boiling point of benzole at  $85^{\circ}5$  ( $186^{\circ}$  F.), and Faraday† found that his “bicarburet of hydrogen” boiled at  $186^{\circ}$  F. ( $85^{\circ}5$  C.) “in contact with glass.” It is difficult to account for these discrepancies, unless the explanation suggested by the clause just quoted from Faraday's account is sufficient.

An experiment made to ascertain the specific gravity of its vapour gave the number  $2\cdot823$ , for which Mitscherlich's probably more correct determination gives  $2\cdot770$ , and calculation  $2\cdot737$ .

Its odour is identical with that of the hydrocarbon yielded by benzoic acid when distilled with an excess of lime. It is extremely inflammable, the vapour arising from it readily taking fire on the approach of a flame near to the surface of the fluid; an enormous quantity of carbon being evolved in the combustion. A current of hydrogen passed through the fluid will burn with an intensely white flame; oxygen similarly treated at the ordinary temperature of the air, forms, with the vapour which it takes up, a mixture of tremendous explosive power. Atmospheric air, charged with the vapour,

\* Locus sup. cit.

† Since these observations were made, by which the boiling point of benzole was thus placed at  $80^{\circ}$  ( $176^{\circ}$  F.), Kopp has published some elaborate researches on certain properties of some fluids (Pogg. Annal. Bd. 72, s. 1 und 223). One of the express purposes of his experiments being the exact determination of boiling points, the greatest confidence is claimed by his results. His statement is, therefore, valuable in confirmation of the fact here noticed. The conclusion which Kopp draws from his observations, which he details at length (op. cit. s. 240), is that the boiling point of benzole is  $80^{\circ}4$  ( $177^{\circ}$  F.), at 760 mm. bar.

will burn with a smoky flame, with a pure white light, or with a beautiful violet-blue flame, according to the size of the jet from which it issues and the velocity with which the stream enters the surrounding air : a given quantity of air taking up more of the vapour than it can itself consume.\*

The specific gravity of the fluid is 0·85. It is extremely mobile, the bubbles, formed upon a surface of it when shaken, breaking instantly before the fluid becomes tranquil : in this respect it differs remarkably from the cognate hydrocarbons having higher boiling points, which retain their bubbles longer, according to their non-volatility, those highest in the scale reflecting most gorgeous iridescent colours from the films of liquid. These latter also exceed benzole in the power of refracting light, though that fluid has this character strongly marked.

*Of some useful properties of benzole.*—Benzole dissolves many substances with extreme readiness and in large quantities, such as many resins, mastic, camphor, wax, fatty and essential oils, caoutchouc and gutta percha. Its volatility gives to its solution of either of the two latter substances, the useful property of drying rapidly and perfectly, so that, when spread on glass or any polished surface, a film of the gum is deposited, which may readily be peeled off in the form of a tough membrane of any required degree of tenuity, and possessing all the properties of the original material. The same solutions varnished on the skin, form admirable artificial cuticles, which have been found useful in cases of wounds and burns, and might probably be very beneficial in some skin diseases.

It dissolves gamboge in smaller quantity, and shell-lac even more sparingly : but it will mix in equal bulks with a saturated solution of lac in wood spirit or alcohol ; this property may be valuable to varnish makers.

Copal and animè yield but slightly to the solvent power of this fluid ; but its vapour in the act of condensation, rapidly dissolves

\* The different volatility of the other coal naphthas which will be here described, (as well as of liquid hydrocarbons generally), is well illustrated by their relative inflammability. Their habitudes in this respect are strikingly different from that of benzole. The fluid boiling about 110° (230° F.) will take fire on its surface, at ordinary temperatures, from a flame, but yields so little vapour to a current of common cool air, that this will only burn with a blue flame. The oils boiling at 145° and 170° (293°—338° F.), afford so little combustible matter to an air stream, as to show no flame at all at the jet, nor will the surface of a stratum of either of them in an open vessel kindle at a match, but will extinguish a burning body plunged into the liquid ; in this behaviour they resemble oil of turpentine which boils at 155° (311° F.).

these resins;\* so that, if fragments of them be suspended in the head of a vessel in which the hydrocarbon is boiling, the vapour, as it condenses on their surfaces, softens and dissolves them, and trickles back into the vessel below, in which a colourless varnish will result, more or less concentrated according to the duration of the process.

Benzole dissolves quinine, depositing it on evaporation in a crystalline form; the condensing vapour dissolves the alkaloid, especially if not recently precipitated, more readily than the boiling liquid. Cinchonine it does not dissolve, but forms with it a bulky gelatinous mass. It dissolves strychnine and morphine, but sparingly.

It dissolves iodine, phosphorus, and sulphur; and, when boiling, takes up the latter in large quantity, of which, however, the greater part crystallizes out as the fluid cools.

It has been found extremely useful in the laboratory as a solvent, in researches in organic chemistry, where the high price, and almost too great volatility, of ether, render a substitute for that agent a frequent desideratum.

It has an interest, too, as offering a cheap and ready source of many of the organic compounds of the benzoic series. Several beautiful bodies, which, from the comparative costliness of the parent materials, had only been obtained previously in very small quantities, may now be prepared in large bulk; such as nitro-benzole, nitrani-line, &c. Dr. Hofmann has recently used coal-tar benzole, prepared by a method which will be described below, as a convenient source of aniline, of which base he has thus produced a large quantity for some researches in which he has been engaged.

The facility with which the vapour of benzole is taken up and retained by the air at its ordinary temperatures, has been mentioned above. This property has been made to do service, with great success, in an apparatus for illumination, in which a stream of air, having passed through a reservoir of the volatile hydrocarbon, is conducted through pipes to the burners, at which, being ignited like coal gas, it yields a light of extreme brilliancy and whiteness.

The property possessed by alcohol and pyroxylic spirit of burning with an almost lightless flame, so opposite to that of the highly carbonized benzole, renders it easy, by properly adjusting a mixture of the volatile oil with either of these spirits, to obtain a fluid which

\* The interesting physical fact, of this property of certain vapours, was pointed out to the writer, as belonging to oil of turpentine, by Mr. Robert Beavan. It seems worthy of more extended knowledge and inquiry. M. Daguerre, in some of his early photographic experiments, found that the vapour of petroleum dissolved certain resins more readily than the liquid.

shall be readily vapourized, and shall yield a flame of any required degree of whiteness. Thus a mixture of one part, by measure, of benzole, and two parts of spirit of sp. gr. about 0·840, forms an excellent fuel for a portable gas-lamp, which supplies itself with vapour by the heat which it generates in combustion. Any excess of spirit diminishes the luminosity of the flame; while too much of the other causes a tendency to smoke. Similar mixtures may be made of benzole with acetone, or with other inflammable liquids poor in carbon. The other fluid hydrocarbons of coal tar are more or less soluble in alcohol and wood spirit, but benzole appears to be more copiously miscible with spirits containing a given amount of water than most of the others; and it is far more so than oil of turpentine.\* The oil requires, of course, a much larger quantity of acetone, than of the spirits† of the ethyle and methyle series, to effect the due reduction of the amount of carbon in the fluid; as will be evident by a comparison of their formulae reduced to a common denominator for hydrogen.

Acetone . . . .	$C_6 H_6 O_2$
Alcohol . . . .	$C_4 H_6 O_2$
Pyroxylic spirit .	$C_3 H_6 O_3$

The inhalation of benzole vapours for the production of insensibility to pain is already on record as effectual. In the instances in which it has hitherto been administered the material prepared from benzoic acid has been found to induce certain phenomena of irritation.‡ Dr. Snow, who has recently tried the effect of coal benzole on mice, has found that it "causes insensibility, but accompanied with convulsive tremors." It is possible, however, that this substance, either

\* The fuel burned in the vapour-lamps of Lüdersdorff, which are in use in some parts of the Continent, consists of oil of turpentine dissolved in alcohol. It is necessary, however, to use very strong alcohol to retain this hydrocarbon in solution, or to distil the two fluids together with certain precautions; and the price of both of these ingredients (of wood spirit sufficiently free from water to dissolve oil of turpentine) is too high in this country to permit this mixture to be consumed. This is not the case with the ingredients mentioned above. The volatility of benzole—so much more nearly similar to that of the spirits—renders it additionally superior to most other hydrocarbons for this purpose.

† It is remarkable that the power of spirits, as solvents for hydrocarbons, seems to bear some inverse relation to the amount of oxygen in the composition of the former, while the solubility of the spirits in water increases in the other direction. Thus oil of turpentine is dissolved by acetone far more readily than by alcohol; and benzole, which is insoluble in alcohol much diluted with water, will expel the water from acetone with which it may be mixed, and will take its place in solution. Again, if to such alcoholic or pyroxylic spirit as will dissolve benzole or some of the other coal naphthas, but refuses to take up oil of turpentine, a small quantity of benzole be added, the spirit will acquire the property of dissolving the oil of turpentine.

‡ Dr. Snow, in Lancet, 1848, February 12; and Professor Simson, in Pharmaceutical Journal, 1848, May.

alone or mixed with the volatile fluids, may yet aspire to become, if not to receive, the "popularis aura."

The promises which benzole makes of utility, are sufficiently numerous to encourage a belief that it may form a special object of manufacture and of commerce. It may be procured to any extent from coal tar or from the light naphtha, in which it has hitherto been "wasting its sweetness on the desert air." If absolute purity be not required, it may be prepared, with very little expense and trouble, either in the laboratory, or, on the large scale, in vast quantities, and by a farther slight outlay of time, any required degree of purity may be ensured in the product. The description of a method which has been found to yield very satisfactory results may be not devoid of interest.

*Of a practical mode of preparing benzole.*—The boiling point of benzole is the same as that of alcohol of sp. gr. 0·825 ( $176^{\circ}$  F. =  $80^{\circ}$  C.); it is evident, therefore, that any of the summary processes of rectification which are practised by distillers in the manufacture of alcoholic spirits, are applicable to the separation of benzole from the less volatile fluids of the naphtha. The method now to be described is, one which extracts nearly the whole of this spirituous hydrocarbon, by a very slight expenditure of time.

The light coal naphtha (of which it is convenient to take a sample which came over at the commencement of the distillation of the tar, which contains the benzole less diluted with substances having higher boiling points) is placed in a metal retort, which is surmounted by an open vessel filled with water, and containing a worm or chamber, into which the vapour of the naphtha passes directly from the retort, and so arranged that the less volatile fluids, which will be condensed in it, will flow back into the retort, or into a separate receiver, while the fluids more volatile than water will pass on in vapour to another condenser, which is kept as cold as possible. The water surrounding the still head will gradually rise in temperature as the operation proceeds, and will at last boil; and when this takes place, (or if the heating of the water be checked at any period of the process, by addition of cold water,) distillation will cease, for no fluid remains in the retort whose vapour is not condensable at the temperature of the head, which can never rise above  $100^{\circ}$  ( $212^{\circ}$  F.). The distillate being rectified a second time in such an apparatus, keeping now the temperature of the head at or a little below  $80^{\circ}$  ( $176^{\circ}$  F.), and reserving the part which comes over before the temperature in the retort has passed  $90^{\circ}$  ( $194^{\circ}$  F.), a large pro-

\* Ure, Dictionary of Chemistry, ed. 1835, art. Alcohol, p. 131.

portion of a very volatile oil will be obtained, which, when exposed to a temperature of— $20^{\circ}$  ( $4^{\circ}$  F.), will become solid to at least half its bulk. Of course, if the apparatus be double, the same result may be obtained by a single operation. A comparatively small quantity of a similar product may be obtained by receiving separately the first two or three gallons that run off from the common stills on the rectification of some hundred gallons of the light naphtha.

This produce should then be agitated with about a quarter of its bulk of oil of vitriol, or, better still, with about one tenth of strong nitric acid, and then, after separation from this agent, with oil of vitriol, as above. It should then be separated from the acid and distilled, (or it may be distilled from the sulphuric acid), reserving again the portion given off below  $90^{\circ}$  ( $194^{\circ}$  F.). The distillate, being tested by agitation with oil of vitriol, should remain perfectly colourless, and the acid should not now acquire a darker colour than a pale straw-brown ; if it acquires a deeper tint, the process should be repeated. When this result is obtained, the oil should be well washed with water, and, finally, with an alkaline solution.

Its farther purification may now be entrusted to its congealing property. It should be exposed to a temperature of about— $20^{\circ}$  ( $4^{\circ}$  F.), (which may be conveniently attained by a mixture of ice and salt) ; the solid portion being then pressed and filtered, the result, after treatment with chloride of calcium, is fit for use.

The use of sulphuric acid in this process is to remove all the basic substances present, to oxidize the brown colouring matter (of which, however, but a small quantity accompanies the most volatile part of the light coal naphtha), and to remove such of the neutral oils as form compounds with oil of vitriol.\* Among these latter, the alliaceous oil, which has been before mentioned, more volatile than benzole, is withdrawn, while the latter entirely resists the action of this acid, even on being boiled with it. The nitric acid assists in the removal of the oxidable substances, and by forming a small quantity of fragrant nitro-benzole, (which is left behind as residue on the distillation of the fluid), improves the odour of the product.

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It has been stated above, that from the light coal naphtha other oils have been obtained in considerable quantity, boiling about certain special temperatures. These have not yet been subjected to the careful

\* The compounds formed with sulphuric acid by some of the oils in the coal naphtha, promise subjects for future examination ; some of them are certainly coupled acids, probably analogous to hypo-sulpho-naphthalic acid, as has been before observed by Bla chet and Sell, (*Annalen der Pharmacie*, Bd. 6, s. 312).

examination which they demand, which, however, it is intended to pursue. Three of these, however, are so decidedly marked as distinct, that they may be mentioned in anticipation of future details.

*Of the oil boiling about 100°-115° (212°-239° F.)*—At a very early stage of the rectifications which have been described in a former section of this paper, an excess of distillate was observed to affect this part of the scale, and the few following degrees. In the later series the point of convergence appeared to lie about 113° (235°·5 F.): a very large fraction has been obtained corresponding to this temperature. This oil has not yet been isolated in a state of absolute purity, so as to claim an analysis: indeed, it has not yet been made the subject of special attention. The basic substance, however, which is obtained from it, by the action of reducing agents on its nitro-compound, proves to consist almost entirely of well crystallized toluidine; so as to leave no doubt that toluole ( $C_{14} H_8$ ) is one of the chief constituents of the light coal naphtha. Dr. Hofmann has used some of the oil, separated from the naphtha by distillation, at the temperature here indicated, as a source of toluidine, for some experiments in which that substance was requisite. The boiling point of benzoène (toluole), which Deville obtained by distilling the resinous part of tolu balsam, was fixed by him at 108° (227° F.)\* Mr. Noad found the toluole which he prepared from toluidic acid to boil between 109° and 110° (228°-230° F.)†

*Of the oil boiling about 140°-145° (284°-293 F.)*—The maximum of distillate, which is most decided in the higher part of the series, is received between 142° and 145° (288°-293° F.) This oil presents all the characters of cumole ( $C_{18} H_{12}$ ). The boiling point of the hydrocarbon, obtained by distilling cuminic acid with an excess of caustic lime, was fixed at first by Gerhardt and Cahours at 144° (291° F.)‡ Mr. F. A. Abel has recently placed it at 148° (299° F.)§ Should the naphtha oil now spoken of prove to be the same substance, its production in large quantity may aid the determination of the question.||

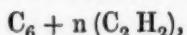
\* Annales de Chimie; sér. 3, t. 3, p. 169. † Philosophical Magazine, vol. 32, p. 32.

‡ Annales de Chimie; sér. 3, t. 1, p. 60. § Philosophical Magazine, vol. 32, p. 66.

|| The existence of toluole and cumole in coal tar is interesting, as shewing the similarity between this substance and the resin tar, in which both of these fluids were detected by Pelletier and Walter, and described by them under the names of retin-naphtha, and retinnyle (Ann. de Chim. t. 67, p. 269). They also found much naphthaline, and described an oil boiling about 240° (230° F.), belonging to the resin tar. It is extremely likely that this last matter was a mixture of oils similar to a part of the neutral fluid of the heavy coal naphtha: and there is little doubt that their metanaphthaline was an impure specimen of paranaphthaline. It has been remarked above, that these authors probably missed some of the hydrocarbons present in their material; so that it is probable that the points of contact between the two productions may be more numerous, if indeed their neutral parts be not altogether identical. Benzole, however, did not appear among the resin oils, although it is by no means unlikely that this oily spirit being present, slipped unnoticed through the hands of the observers.

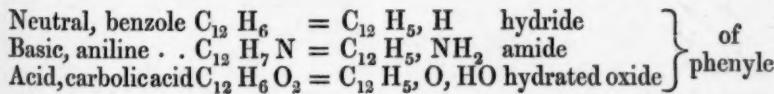
*Of the oil boiling about 170°-175° (338°-347 F.)*—The next favourite point lies between 170° and 172° (338°-342° F.); and the fluid which distils over at this temperature, bears so strong a resemblance in odour and in other properties to cymole ( $C_{20} H_{14}$ ), the boiling point of which Mr. Noad observed to be at 171°·5 (341° F.),\* as to induce the belief that this body is identical with the hydrocarbon existing in cumin oil. This oil, though by its nature (sp. gr. 0·857) referrible to the light naphtha, in which it is found, as above remarked, only in small proportion, is largely contained in the heavy coal naphtha, from which it is intended to prepare it, hereafter, for examination.

If these latter hydrocarbons be correctly assigned to the places of toluole, cumole, and cymole, it will be an interesting fact that coal tar contains, among its chief constituents, the only four members yet known of the series of hydrocarbons which are represented by the formula



in which  $n$  represents successively the order of natural numbers, the lowest known term of which is that in which  $n = 3$ ,—(Benzole). It may seem, too, not improbable that the gap, which chemistry has not yet filled (where  $n = 5$ ), the boiling point of whose corresponding oil would probably lie between that of toluole and cumole, may yet find its occupant in the coal naphtha. It may be hoped, too, that this fruitful source of the compounds alluded to, may not long leave, *sub judice*, the theory of the successive increments of temperature, necessary for ebullition, which is due to each successive factor, of  $C_2 H_2$ , introduced into the composition of the fluids.

Nor is the remark unworthy of citation here, that a close relation seems to exist between three of the tar compounds—one from each of the three classes—thus,



It may be useful to exhibit the constitution of coal tar in a tabular form, representing the boiling points of the various substances contained in it, which will indicate the part of the products in which any one of the substances is to be looked for when the distilling temperature is indicated by a thermometer.

\* Philosophical Magazine, vol. 32, p. 18.

## SUBSTANCES CONTAINED IN COAL TAR.

Centig. Therm. scale.	Neutral.	Basic.	Acid.	Tar Pro- ducts.
50 ..			? Pyrrol, ?	
-				
-				
70				
80 ..	Benzole, $C_{12}H_6$			
-				
-				
100 ..				
111 ..		Picoline, $C_{12}H_7N$		
113 ?..	Toluole, $C_{14}H_8$			
-				
-				
148 ?..	Cumole, $C_{18}H_{12}$			
-				
-				
171 ..	Cymole, ?, $C_{20}H_{14}$			
182 ..		Aniline, $C_{12}H_7N$		
187 ..			{ Carbolic acid Hydrate of phenyle } $C_{12}H_6O, HO$	
200 ..				
-				
212 ..	Naphthaline, $C_{20}H_8$			
220 ..				
239 ..		Leukoline $C_{18}H_8N$		
-				
-				
280 ..				
300 ..				
?	Paranaphthaline, $C_{30}H_{12}$ ?			
?	Pyrene ?, $C_{15}H_6$ ?			
?	Chrysene ?, $C_{12}H_6$ ?			
				Pitch.
				Heavy-oil, or "Dead-oil."
				Light-oil, or "Naphtha."

XXII.—*Researches on the Volatile Organic Bases.* By A. W. HOFMANN,  
PH.D. Professor at the Royal College of Chemistry.

II.—ON THE ACTION OF IODINE ON ANILINE.

The changes which organic bodies undergo when submitted to the action of bromine and of chlorine, have of late been examined with great care by various chemists; and it must be admitted, by every body who has followed these investigations with attention, that they have thrown much light on various parts of organic chemistry.

The metamorphoses produced by these two elements, so remarkable for their powerful affinities, are generally of so strongly marked a character that, in the study of the derivatives thus obtained, the nature and constitution of a new body frequently unfold themselves in a most surprising manner. Chlorine and bromine have become in fact general agents in organic investigations. Their mode of action is known to us, based as it is, in most cases, upon their great affinity for hydrogen.

Less attention has hitherto been bestowed upon the action of iodine on organic bodies. The affinity of this element for hydrogen being much weaker, decompositions ensue with far greater difficulty.

Wöhler and Liebig, in their series of experiments on the radical of benzoic acid\*—the first researches, perhaps, in which the influence of the saltformers on organic substances was investigated—found that, while part of the hydrogen in oil of bitter almonds could be eliminated with great facility by chlorine or by bromine, the corresponding iodine-compound—iodide of benzoyle—could only be obtained indirectly, viz., by the action of chloride of benzoyle on iodide of potassium, iodine being dissolved with facility in oil of bitter almonds, but no decomposition taking place. In accordance with this observation, it was established by various subsequent researches, that many organic substances by themselves may be brought into contact with iodine without undergoing the slightest change, but that decomposition can be effected with the co-operation of alkalies. In these cases, the action is a common process of oxidation, an alkaline iodide being formed, while the organic body, under the influence of the liberated oxygen, is resolved into more simple compounds. The transformations of fusel oil, by means of iodine and potash, into valerianic acid, of salicine into salicylous acid, of amygdaline into oil of bitter almonds, are well-known instances of this mode of action. To these we may add the deportment of iodine with several of

\* Liebig's Annalen, vol. III. p. 249.

the volatile oils, such as oil of anise and fennel oil, which has only recently been investigated by Dr. Will.\* Here, likewise, iodine exercises a feebly oxidising action, substances richer in oxygen but free from iodine being formed. In some cases, we also find the iodine combining with the newly-formed products; pyroxylic spirit, alcohol, citric acid, sugar, and several other substances, yield, as is well known, in this manner, iodoform with various other products.

Moreover, we have a great variety of instances in which iodine is found to combine directly with organic bodies. Whether the blue compound of iodine and starch be a chemical combination or not, the entrance of iodine in this case is certainly not accompanied by an elimination of hydrogen; and we can scarcely adopt any other view respecting iodide of clayle, if we take into consideration the mode of formation of this body, and the facility with which it is again resolved into iodine and olefiant gas.

Analogous facts have been elicited with reference to the deportment of iodine with organic bases, which has been the subject of several investigations. Pelletier,† who first directed his attention to this question, arrived, by a series of experiments on strychnine, brucine, quinine, and cinchonine, at the conclusion that these bases were capable of combining directly in various proportions with iodine, an opinion which appeared to be confirmed by some subsequent experiments of Regnault.‡ The products thus obtained would correspond to the combinations of iodine with ammonia, described by Gay-Lussac, Bineau, and Millon. The analytical numbers given in Pelletier's investigation are, however, very unsatisfactory, and Regnault has paid but little attention to the subject.

The same question was again taken up by Bouchardat.§ According to whose experiments, the details of which, however, do not appear ever to have been published, these products should be considered as combinations of the hydriodates with iodine, whose representative in the ammonium series we find to be iodinated iodide of ammonium. It is possible that *both* classes of compounds exist: the subject requires further investigation.

If all the researches on the action of iodine on organic substances be glanced over, it will be found that there is scarcely a single instance known, in which iodine does, like chlorine and bromine, eliminate and replace hydrogen, the fundamental properties of the compound

\* Liebig's Annalen, vol. LXXV. p. 230.

† Annales de Chimie et de Physique, 2ème sér. LXIII. p. 164. Liebig, Annalen, vol. XXII. p. 113.

‡ Ann. der Chemie Pharm. vol. XXIX. p. 58.

§ Comptes Rendus, t. IX. p. 475.

remaining unaltered. These considerations gave rise to some experiments on the behaviour of iodine with aniline, which I wish to communicate to the Society in the following pages.

The action of chlorine and bromine on aniline, as is well known, is very powerful. By their agency, it appears, that those products of substitution only can be obtained in which the whole of the replaceable hydrogen in the original aniline has been eliminated, and which have lost their basic properties. The anilines in which a smaller quantity of hydrogen is substituted, have, however, likewise been obtained by other processes, viz., by the action of alkalies on chlorinated and brominated isatine.\*

The adoption of a similar method seemed to promise the preparation of iodinated aniline. Iodisatine, however, being as yet unknown, and considering the far less powerful affinity of iodine for hydrogen, I resolved to ascertain whether the desired object might not be accomplished by the direct treatment of aniline with iodine.

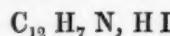
*Action of iodine on aniline.*—Iodine dissolves in anhydrous aniline, forming a dark brown liquid, and a rapid evolution of heat indicates at once a lively chemical reaction. If an excess of iodine has been avoided, long needles soon appear, surrounded by a brown mother-liquor. These crystals are exceedingly soluble in water and in alcohol, but less so in ether, by which liquid they may be separated from a great portion of the mother-liquor. Solution in water and ebullition with animal charcoal, and subsequent recrystallization, render them perfectly pure. The quantitative analysis proves them to be pure hydriodate of aniline.

This salt not having been previously analyzed, an iodine determination was made,

0·2856 grm. of hydriodate of aniline gave

0·3025 grm. of iodide of silver.

The formula



requires

	Theory.	Experiment.
1 equiv. of aniline . . . . .	93·00	42·21
1 equiv. of hydriodic acid . . . . .	127·36	57·79
1 equiv. of hydriodate of aniline 220·36	100·00	57·53

The dark brown mother-liquor of this salt is a mixture of various substances: it contains, besides, some hydriodate of aniline, a certain

\* Memoirs of the Chemical Society, vol. II. p. 266.

quantity of free iodine, which can be removed by alkalies, a brown product of decomposition, insoluble in acids and in alkalies, containing both aniline and iodine, and, lastly, the hydriodate of an iodinated base, to which, from its composition, the name of *iodaniline* belongs. The separation of the latter is easily effected by means of hydrochloric acid.

*Preparation of iodaniline.*—Anhydrous aniline is intimately mixed with one and a half times its weight of iodine. The brown liquid thus obtained solidifies after a very short time into a crystalline mass containing the above-mentioned substances, among which, however, iodaniline greatly preponderates. On the addition of common hydrochloric acid (sp. gr. 1·11) to this mass, the hydriodates are decomposed, difficulty soluble hydrochlorate of iodaniline remaining in the residue, while hydrochlorate of aniline enters into solution. Hydrochloric acid of greater strength should be avoided, as it would precipitate likewise some hydrochlorate of aniline. The salt, which is still much coloured, having been washed with hydrochloric acid for a short time, is now dissolved in boiling water: this solution deposits, on cooling, beautiful ruby-red very distinct crystals of hydrochlorate of iodaniline, containing still a certain amount of free iodine. By repeated crystallizations from boiling water, these crystals become constantly paler, part of the free iodine remaining each time in solution. It is scarcely probable that these coloured crystals are combinations of hydrochlorate of iodaniline and iodine in chemical proportions. I have not, however, any experimental evidence to the contrary. Possibly some of Pelletier and Bouchardat's compounds may be of a similar kind. It is scarcely possible to remove entirely the free iodine, which adheres to them with great pertinacity by mere crystallization; it may be separated, however, with facility by treatment with animal charcoal. By this process, not only the iodine, but also the brown product of decomposition is nearly altogether removed. A colourless solution is obtained, which, filtered while hot, deposits, on cooling, a large quantity of iridescent plates of a hydrochlorate, very similar in appearance to benzoic acid.

On the addition of caustic ammonia to a solution of this salt, a beautifully white precipitate of iodaniline is obtained, which is, however, not yet absolutely pure; it is still contaminated with small quantities of a yellowish substance, containing iodine, (frequently also with traces of phosphate of lime from the charcoal), from which it may, however, easily be separated by solution in alcohol, in which this yellow substance is quite insoluble. On mixing the alcoholic solution with water, a white crystalline mass of perfectly pure

iodaniline is instantly thrown down ; by evaporation on a water-bath, the base is separated in the form of yellow oily drops, which soon solidify to a crystalline mass.

The brown mother-liquor, filtered from the crude hydrochlorate of iodaniline, deposits, after a time, large crystalline plates, of an emerald-green colour, which possess the peculiar metallic lustre of the wing-covers of certain beetles. These crystals remain perfectly unaltered while in contact with the acid mother-liquor, but cannot be dried without undergoing change. The hydrochloric liquid being drained from them, they instantly become brown on exposure to the air. On the addition of water, the greater portion is rapidly dissolved, forming a light brown solution, on which a few oily drops still float. If this solution be boiled with animal charcoal, it becomes colourless, and deposits, on cooling, crystals of pure hydrochlorate of aniline, mixed perhaps with a small quantity of hydrochlorate of iodaniline.

I could not find a method of procuring the green crystals in a state fit for accurate analysis. In order to obtain an idea of their nature, some of the crystals were rapidly collected, purified and dried, as far as was practicable, by pressure between folds of bibulous paper, and kept in *vacuo* for a few days, when a small quantity of iodine was evolved. The solution of the substance thus prepared, was treated with hydrosulphuric acid, to convert the last trace of iodine into hydriodic acid, it was then boiled and thrown down with nitrate of silver. The precipitate was chloride of silver, mixed with traces only of iodide.

0·3200 grm. of the emerald crystals gave

0·3323 grm. of silver-salt.

If the silver-salt had been pure chloride of silver, the crystals would contain 25·68 per cent of chlorine, the amount in hydrochlorate of aniline being 27·41 per cent.

From this approximative analysis, as well as from the general behaviour of the crystals, it is evident that they are in fact nothing but hydrochlorate of aniline, which have carried down a small quantity of iodine,\* by which their beautiful appearance is produced.

Among the products of the action of iodine on aniline, I have mentioned several times a brown compound containing aniline

\* In an analysis of this kind, the determination by means of nitrate of silver should have yielded rather an excess of chlorine, the small quantity of iodine having been calculated as chlorine. The presence, however, of a small amount of hydrochlorate of iodaniline (containing only 13·93 per cent of chlorine,) and the incompleteness of the method of desiccation, are sufficient to explain the small loss in the analysis.

and iodine, which is insoluble in acids and in alkalies. This substance is likewise insoluble in water. Alcohol and ether dissolve it; but it does not crystallize from any of these solutions; it is not volatile without decomposition. As nothing evinced the individuality of the substance, I did not investigate it any further.

*Composition of iordaniline.*—The analysis of iordaniline did not present any difficulties. Two determinations of the carbon and hydrogen, with one estimation of the iodine, were sufficient to establish the composition of the new body.

By burning the substance with oxide of copper, the following results were obtained:

- I. 0·4144 grm. of iordaniline gave
  - 0·5000 " " carbonic acid and
  - 0·1055 " " water.
- II. 0·2149 " " iordaniline gave
  - 0·2621 " " carbonic acid and
  - 0·0553 " " water.
- III. 0·4970 " " iordaniline converted into iodide of calcium by combustion with lime and precipitated by nitrate of silver, gave:
  - 0·5335 grm. of iodide of silver.

Per centage composition:

	I.	II.	III.
Carbon . . .	32·90	33·26	—
Hydrogen . . .	2·82	2·85	—
Iodine . . .	—	—	57·87

These numbers exactly represent the composition of moniodaniline



as the following comparison with the theoretical numbers will show:

	Theory.	Experiment.
12 eq. of carbon . . .	72·00	32·97
6 " of hydrogen . . .	6·00	2·74
1 " of iodine . . .	126·36	57·86
1 " of nitrogen . . .	14·00	6·43
1 " of iordaniline . . .	218·36	100·00

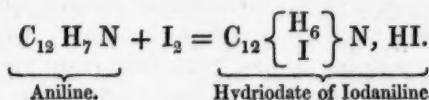
The correctness of this formula was satisfactorily controlled by

several determinations of the equivalent of the base as resulting from the analysis of its various salts.

\* Two determinations of platinum in the platinum-salt, which I shall mention hereafter, gave a mean per centage of 23.14 of platinum.

Equivalent by experiment . . . .	220.26
Equivalent by theory . . . .	218.36

The formation of iodaniline is effected by a simple process of substitution :



*Properties of iodaniline.*—Iodaniline resembles aniline in most respects, and is even more similar to chloraniline and bromaniline. It is characterized by the same pleasant, somewhat vinous odour, the same aromatic and burning taste, the same solubility in alcohol, ether, pyroxylic spirit, acetone, bisulphide of carbon, and fatty and etherial oils. In water it dissolves but very little. These solutions have not the slightest action on vegetable colours. Iodaniline is heavier than water.

When I first obtained this compound, I expected to see it crystallize in octohedrons, an anticipation which appeared to be supported by the crystalline form of chloraniline and bromaniline, and the generally assumed isomorphism of chlorine, bromine and iodine. But I have vainly searched the different crystallizations of iodaniline for octohedrons; from all the solutions which I tried, iodaniline was invariably deposited in prismatic crystals; from a boiling aqueous solution, it separates after some time in long hair-like needles. The crystalline mass obtained by the solidification of the fused base likewise exhibited no cleavage of an octohedron.

The crystals of iodaniline fuse far below the boiling-point of water into a yellow oil. A small quantity of this substance, heated in a water-bath, was completely fused at 60° C. (140° F.); at the moment of solidification the thermometer indicated 51° C. (124° F.) Sometimes the base remains liquid for a long period, even at common temperatures; it is then usually solidified at once by agitation. At higher temperatures iodaniline may be volatilized without much decomposition. With the assistance of aqueous vapour, it distils with the greatest facility. The vapour of the base burns with a brilliant smoky flame.

Like aniline and its chlorinated and brominated relatives, iodani-

line imparts an intense yellow colour to fir-wood and the pith of the elder-tree; but it does not communicate the characteristic violet colour to hypochlorite of lime; a solution of this reagent on being mixed with iodaniline assuming only a slight red tint; nor is the aqueous solution altered by chromic acid. The dry and fused substance, however, when in contact with solid chromic acid, is destroyed with violence, but not inflamed like aniline and bromaniline.

*Compounds of iodaniline.*—The salts of iodaniline crystallize with the same facility as those of aniline. They are generally less soluble than the latter. By the entrance of iodine, the basic properties of aniline have been considerably weakened. A solution of aniline in water decomposes the salts of iodaniline with facility, and whilst aniline precipitates several metallic oxides, iodaniline is only capable of displacing alumina from its salts. The salts of oxide of zinc and sesquioxide of iron are not decomposed by iodaniline. With sulphate of copper a yellowish precipitate is produced, which is evidently a double salt.

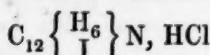
*Hydrochlorate of iodaniline.*—This salt is but slightly soluble in cold water. The aqueous solution is precipitated nearly entirely by concentrated hydrochloric acid. From boiling water the salt crystallizes in plates or thin broad needles, which dissolve in alcohol, but are insoluble in ether.

Analysis gave the following results :

0·4531 grm. of hydrochlorate of iodaniline.

0·2573 „ of chloride of silver.

The formula :



requires the following numbers :

	Theory.	Experiment.
1 equiv. of iodaniline . . . . .	218·36    85·69	—
1 „ „ hydrochlorate acid . . .	36·50    14·31	14·44
1 „ „ hydrochlorate of iodaniline	254·86    100·00	

*Hydrobromate of iodaniline.*—This salt resembles the preceding in every respect.

*Hydriodate of iodaniline* forms a radiated crystalline mass, far more soluble than the preceding salts. It is very rapidly, decomposed.

*Sulphate of iodaniline.*—This salt crystallizes in white brilliant scales. With respect to its solubility, it resembles the hydrochlorate precisely. The solution of this salt appears to be decomposed by ebullition; there remains, at least, a small quantity of a substance, which is completely insoluble in water.

Three determinations of the sulphuric acid, in specimens of different preparations, gave a slight excess above the theoretical quantity.

I. 0·5249 grm. of sulphate of iodaniline gave:

0·2367 " " " barytes

II. 0·3440 " " " iodaniline gave:

0·2037 " " " barytes

III. 0·3440 " " " iodaniline gave:

0·1577 " " " barytes

which quantities afford the following per centage:

	I.	II.	III.
Hydrate of sulphuric acid . . . . .	18·94	19·56	19·24

The formula:

requi res	$C_{12}\left\{ \begin{smallmatrix} H_6 \\ I \end{smallmatrix} \right\} N, H SO_4$	Theory.		Mean of experiments.
		218·36	81·68	
1 equiv. of iodaniline . . . . .	218·36	81·68	—	
1 " " hydrate of sulphuric acid	49·00	18·32	19·24	
1 " " sulphate of iodaniline .		<u>267·36</u>		

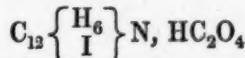
*Oxalate of iodaniline.*—This salt forms splendid long, flattish needles, which, like the hydrochlorate, are difficultly soluble in water and in alcohol, and insoluble in ether.

The analysis of this salt gave the following results:

0·5020 grm. of oxalate of iodaniline gave

0·0969 " " carbonate of lime.

The formula:



requires the following numbers:

	Theory	Experiment.	
1 equiv. of iodaniline . . . . .	218·36	82·92	—
1 " " hydrate of oxalic acid .	45·00	17·08	17·37
1 " " oxalate of iodaniline .	<u>263·36</u>	<u>100·00</u>	

*Nitrate of iodaniline.*—This salt crystallizes from water in beautiful hair-like needles, often some inches in length. It is more soluble in water, especially when boiling, than any other salt I have examined. It is likewise easily soluble in alcohol and in ether. Its solution is not precipitated by nitrate of silver.

*Bichloride of platinum and iodaniline.*—The hydrochlorate of the base yields a beautiful orange-yellow crystalline precipitate with bichloride of platinum, which may be easily purified by washing with ether.

The following are the experimental numbers obtained by analysis:

I. 0·2675 grm. of platinum-salt gave :

0·1650 " " carbonic acid, and

0·0451 " " water.

II. 0·2771 " " platinum-salt gave :

0·0643 " " platinum.

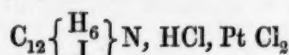
III. 0·1218 " " platinum-salt gave :

0·0281 " " platinum,

per centage, composition :

	I.	II.	III.
Carbon . . . . .	16·82	—	—
Hydrogen . . . . .	1·87	—	—
Platinum . . . . .	—	23·20	23·07

corresponding exactly with the formula :



as may be seen from the following table:

	Theory.	Experiments.
12 equiv. of carbon . . . . .	72·00	16·95
7 " " hydrogen . . . . .	7·00	1·64
1 " " nitrogen . . . . .	14·00	3·29
1 " " iodine . . . . .	126·36	29·79
3 " " chlorine . . . . .	106·50	25·09
1 " " platinum . . . . .	98·68	23·24
" " platinum-salt . . . . .	424·54	100·00

A solution of hydrochlorate of iodaniline yields a scarlet precipitate with bichloride of gold, which is, however, rapidly decomposed.

The following table embraces the iodaniline compounds which have been analysed :

Iodaniline . . . . .	$C_{12} \left\{ \begin{matrix} H_6 \\ I \end{matrix} \right\} N$
Hydrochlorate of iodaniline .	$C_{12} \left\{ \begin{matrix} H_6 \\ I \end{matrix} \right\} N, H Cl$
Sulphate of iodaniline . . .	$C_{12} \left\{ \begin{matrix} H_6 \\ I \end{matrix} \right\} N, H SO_4$
Oxalate of iodaniline . . .	$C_{12} \left\{ \begin{matrix} H_6 \\ I \end{matrix} \right\} N, H C_2 O_4$
Platinum salt . . . . .	$C_{12} \left\{ \begin{matrix} H_6 \\ I \end{matrix} \right\} N, HCl, Pt Cl_2$

*Products of decomposition of iodaniline.*—The metamorphoses which the iodinated base undergoes, when treated with various chemical agents, are very analogous to those of aniline ; I have consequently studied them but cursorily.

Iodaniline, when gently heated with *potassium*, is decomposed with violence ; iodide and cyanide of potassium being produced.

A concentrated aqueous, or alcoholic solution of *potash* has no effect on iodaniline, not even at the boiling temperature.

*Chlorine* gives the same products with iodaniline, as with aniline itself ; viz., trichloraniline and chlorophenisic acid. The iodine, in this case, is evolved in the form of chloride.

*Bromine* acts in a similar manner. On adding a few drops of bromine to an alcoholic solution of iodaniline, a crystalline mass is produced, which is pure tribromaniline, the whole of the iodine being evolved in the form of bromide.

In order to establish this fact, a bromine determination of the tribromaniline thus formed was made.

0·1200 grm. of substance, heated with lime, &c., gave :

0·2076 „ „ bromide of silver.

	Theory.	Experiment.
Per centage of bromine in tribromaniline . . .	72·28	72·68

This result was to be expected. In inorganic chemistry, we always find iodine expelled by chlorine and bromine. And among organic substances, similar cases have also been observed. According to Bouchardat's experiments, iodoform is easily converted into chloroform or into bromoform, when acted on by chlorine or by bromine.

A mixture of *chlorate of potash* and *hydrochloric acid* convert iodaniline into chlorokinone (chloranil) and chlorophenisic acid.

Iodaniline is rapidly destroyed by boiling *nitric acid*. In this pro-

cess the iodine is set free, and from the solution, scaly crystals of nitrophenisic acid are deposited on evaporation.

One peculiar decomposition I have still to mention.

Chemists are acquainted with the ingenious process which was devised by M. Melsens for substituting hydrogen in the place of chlorine in chloracetic acid. This acid, dissolved in water, is treated with a weak amalgam of potassium, and whilst the chlorine atoms are seized, as it were, by a portion of the potassium, the empty spaces become occupied by a corresponding number of atoms of hydrogen, liberated by the action of the same metal on the water. This process promises to become particularly important when employed in cases where the hydrogen term is still wanting. When Dr. Kolbe was in London, we made a few experiments of this kind together. Amongst other substances, we acted with amalgam of potassium on chloraniline and bromaniline, which, as was to be expected, are re-converted into aniline with the greatest facility. M. Melsens told me, that in performing the same experiments, he arrived at the same results.

Iodaniline I find likewise undergoes a similar change. The nitrate of this base, when brought into contact with amalgam of potassium, is at once decomposed, and the solution yields immediately a yellow precipitate with nitrate of silver. Only a small quantity, however, of aniline is reproduced in this process : the larger portion undergoes a further change, being converted into a yellow crystalline compound, of aromatic odour, the composition of which I have not yet ascertained.

The reproduction of aniline from iodaniline succeeds also with nascent hydrogen only. For effecting this, it is sufficient to heat an acid solution of sulphate of iodaniline, with some scraps of zinc, for a few minutes ; starch paste indicates at once the liberation of iodine in the solution, while the addition of potash, and agitation with ether, separates the aniline, which may now be detected by a solution of hypochlorite of lime.

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The action of *chlorine*, *bromine*, *iodine* and *cyanogen* on aniline, affords an interesting illustration of the decreasing affinities which these radicals manifest for hydrogen.

By treating aniline with *chlorine*, the molecular arrangement of this body is nearly entirely destroyed ; almost the whole is converted into chlorophenisic acid, a body only loosely connected with the original atom, while very small quantities of neutral trichloraniline are formed.

*Bromine* likewise acts very powerfully on aniline ; yet its action is limited to a process of substitution, not less than three equivalents of hydrogen being replaced by bromine, in the formation of neutral tribromaniline.

With *iodine*, as we have seen, we may obtain a compound in which only one equivalent of hydrogen is replaced by iodine, the product retaining the basic properties of the original atom.

*Cyanogen*, finally, is no longer capable of eliminating hydrogen. It directly combines with aniline, producing a compound in which the original character of aniline has not been altered.

June 19, 1848.

John Thomas Cooper, Esq., Vice President, in the chair.

Mr. Thomas Taylor exhibited and described a small hot-air chamber, which he had devised for the purpose of drying precipitates, &c., in the laboratory.

The following papers were read :

**XXIII. On a New Method for the Quantitative Determination of Nitric Acid, and other Compounds of Nitrogen, by J. C. NESBIT, Esq., F. G. S., &c.**

It has long been felt as a great evil by chemical analysts that no good, efficient, and easy plan for the determination of nitric acid and some of the compounds of nitrogen has yet been made known, and that, consequently, the analysis of these substances is a matter of considerable difficulty and trouble. Any attempt towards the solution of this problem will, it is to be hoped, receive a favourable consideration from many who have experienced the need of an easier plan.

The method, which is the subject of this paper, depends upon the possibility of converting, by means of nascent hydrogen, an equivalent of nitric acid, or of any nitrate or other body containing an equivalent of nitrogen, into an equivalent of ammonia ; a substance of very easy quantitative determination.

It was long ago observed, that when dilute nitric acid is allowed to act upon tin filings, ammonia may be detected in the solution of the metal. The same was afterwards observed with iron. Kuhlman\*

\* *Annales de Chemie*, vol. LXVII, p. 209.

has still further generalized these observations by proving, "that all the metals capable of decomposing water give a certain quantity of ammonia when they are placed in contact with weak nitric acid."

More recently, Kuhlman\* has published a number of experiments, showing, under various circumstances, the production of ammonia by nascent hydrogen in the presence of one or other of the nitrates.

Thus he shows, that when dilute sulphuric or hydrochloric acid in contact with iron or zinc, is in the act of evolving hydrogen, the addition of a nitrate causes the evolution of gas to cease for a while, and that afterwards, ammonia may be found in the solution.

It is evident from this, that the nascent hydrogen unites with the oxygen of the nitric acid to produce water, and also with the nitrogen to produce ammonia. For this purpose, 8 equivalents of hydrogen are required to convert one equivalent of nitric acid,  $\text{NO}_6\text{H}$  into 6 equivalents of water,  $6\text{HO}$ , and one of ammonia,  $\text{NH}_3$ , or with the addition of one atom of water,  $\text{NH}_4\text{O}$ , oxide of ammonium.

The experiments of Kuhlman, which are all qualitative, do not appear to have been carried further than was necessary to illustrate his views of nitrification; and they do not therefore show the extent to which this conversion is carried, and whether the whole of the nitrogen can be made to assume the form of ammonia.

A number of experiments have in consequence been instituted in our laboratory, which have proved that, with proper precautions, the whole of the nitrogen in the nitrates and in nitric acid, may easily be made to assume the form of ammonia, and thus be rendered easy of determination.

If ten grains of a salt, such as nitrate of potash, be taken for analysis, about 200 or 300 grains of thin, clear fragments of zinc are put into a small flask, to which a portion of water is added. From half an ounce to three quarters of an ounce of hydrochloric acid, sp. gr. 1.17, must be poured out into a small measure, and about one tenth part added to the zinc and water. When effervescence has fairly commenced, a portion of the nitrate, previously dissolved in a small quantity of water, is added to the mixture. The temperature of the whole must, if necessary, be kept low, by placing the vessel in cold water. After a short period, a little more acid is added, and then a little nitrate, until all the solution of the nitrate with the washings is poured in, and about one fourth of the acid is left. Care should be taken that, for the first hour, the effervescence is slow. When the whole of the solution of the nitrate is poured in, the remainder of the acid

\* *Expérience Chimique et Agronomique*, p. 98.

must be added from time to time, and the whole left until effervescence ceases. The liquid is then carefully separated from the undissolved zinc, which is well washed with the smallest quantity of water, and the whole distilled with a proper quantity of hydrate of lime, or occasionally, a little potash; the ammonia being collected in a proper condenser, similar to Liebigs' five-bulb apparatus. The great danger to be avoided consists in allowing the hydrogen to be liberated too rapidly, by which means so much heat is generated as to cause a portion of the nitrogen to escape in the form of binoxide of nitrogen. It is useless to point out that the hydrochloric acid must contain no salt of ammonia.

The ammonia is determined in our laboratories by a method similar to that of Dr. Ure, which admits of considerable exactness, viz., by the use of a solution of litmus and a neutralizing acid of known constitution. The dilute sulphuric acid used, has a sp. gr. of about 1·0327; 1000 grain measures of which contain exactly an equivalent in grains of sulphuric acid. This quantity, therefore, will exactly neutralize an equivalent of any alkali.

The acid can always be easily kept at the proper strength, by means of two hydrostatic bulbs made, the one to float, and the other to sink, in the acid of proper specific gravity.

A graduated tube is filled with the acid, a small quantity of a solution of litmus is poured into a good-sized evaporating-dish, and then a portion of the ammonia-water from the receiver. The acid is cautiously added until the mixture becomes red, more ammonia is added until it turns blue, then a little more acid; and, lastly, the receiver is rinsed out, and the acid carefully dropped in until the blue colour of the mixture just changes to red, when the number of drops of acid that have been used must be read off. The number of drops of acid, multiplied by the equivalent of ammonia and divided by 1000, will give the amount of ammonia present in the body under examination. In the case of a nitrate being employed, the number of drops of acid, multiplied by the equivalent of the nitrate under examination and divided by 1000, will give the amount of the pure nitrate used. A similar calculation is made for nitric acid.

The following experiments will demonstrate the accuracy of this method for the determination of the nitrates, and its applicability to numerous difficult cases. For most of the results I am indebted to those of my pupils whose names are attached to their respective analyses.

TABLE OF EXPERIMENTS ON THE COMPLETE CONVERSION OF NITRIC ACID INTO AMMONIA.

Substance taken.	Drops of acid to neutralize the produced ammonia.	Substance by calculation.	Nitric acid by theory.	Nitric acid by calculation from experiment.	
1 15 grs. pure nitre	148	14.99	8.01	8.01	J. C. Nesbit.
2 15 " ditto	148	14.99	8.01	8.01	J. Bailey.
3 8 " ditto	80	8.19	4.27	4.33	J. Gater.
4 15 " ditto	148	14.99	8.01	8.01	J. Bailey.
5 5 " ditto	49	4.96	2.67	2.65	ditto.
6 5 " ditto	49	4.96	2.67	2.65	J. Gater.
7 15 " ditto	148	14.99	8.01	8.01	ditto.
8 5 " ditto	50	5.06	2.67	2.70	E. Lane.
9 15 " ditto	148	14.99	8.01	8.01	J. Bailey.
10 5 " ditto	49	4.96	2.67	2.65	ditto.
11 10 " nitre and } 11 95 " salt }	99	10.02	5.34	5.36	ditto.
12 15 " nitre and } 12 95 " salt }	10	15.19	8.01	8.12	ditto.
13 5 " nit. baryta	38	4.97	2.06	2.05	J. Gater.
14 5 " nitre	49	4.96	2.67	2.65	ditto.
15 5 " nit. lead	30	4.97	1.63	1.62	ditto.
16 5 " nit. baryta	38	4.97	2.06	2.05	J. Blyth.

Experiments have been instituted with some other compounds of nitrogen, but want of leisure has prevented the completion of the investigation.

With the yellow prussiate of potash not a trace of ammonia was found, but there was a small quantity in a specimen of the red prussiate, for whose purity, however, I dare not vouch.

Some experiments have also been made with vegetable alkalies, and I apprehend that eventually, by the employment of nascent hydrogen, a much greater knowledge of the intimate constitution of some organic bodies will be obtained.

Caffeine and quinine, when subjected to this process, furnished ammonia; and in one experiment with urea, one half of the nitrogen was liberated in the form of ammonia, whilst the other, doubtless remained as a cyanogen compound.

I have had no opportunity of trying this process with the nitrites,

hypo-nitrates, &c., but I have no doubt that it will serve as an easy method for their analysis.

I have hastened to lay this method before the Society, because my other engagements are such as to prevent me at this moment from pursuing the subject to the extent that is desirable, and because I am in hopes that some gentlemen, who may enjoy more leisure, may be inclined to follow up the subject.

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XXIV. *Researches on the Volatile Organic Bases, by DR. A. W. HOFMANN, Professor at the Royal College of Chemistry.*

III. ACTION OF CHLORIDE, BROMIDE, AND IODIDE OF CYANOGEN  
ON ANILINE.

MELANILINE, A NEW CONJUGATED ALKALOID.

The original object of my experiments on the action of cyanogen upon aniline was the formation and the study of a cyanogen base, corresponding to chloraniline, bromaniline, iodaniline, and nitraniline.

These experiments, which I have lately communicated to the Society,\* have proved that the compound in question cannot be obtained in the manner indicated, but that the cyanogen combines directly with the aniline. The production of this body appeared, however, of sufficient interest to encourage me to apply some further methods promising a different result.

The idea naturally suggested itself to try the action of cyanogen associated with an element possessing an eminent affinity for hydrogen. There seemed to be a chance of thus eliminating hydrogen, the place of which would then be open for the cyanogen.

The gaseous chloride of cyanogen of Gay-Lussac, and Serullas' corresponding bromide, appeared to be compounds likely to produce the effect desired.

*Action of gaseous chloride of cyanogen on aniline.*—The gaseous chloride of cyanogen is obtained, as is well known, either by passing a current of chlorine into a solution of hydrocyanic acid, or by the action of this gas on moistened cyanide of mercury.

In the course of my experiments I have employed both methods, but as I soon found that the presence of water directly influenced the nature of the products arising from aniline, I have generally preferred the latter plan, which yields the chloride of cyanogen in a nearly dry state, and free from hydrochloric acid.

\* Quarterly Journal of the Chemical Society, vol. 1, p. 159.

In treating aniline with chloride of cyanogen, it is necessary to avoid an admixture of free chlorine, which complicates the process, by simultaneously producing trichloraniline and chlorophenisic acid; it is important, therefore, to use a slight excess of cyanide of mercury, and not to begin the operation until the bottles previously filled with chlorine have become perfectly colourless.

In order to protect myself against the chloride of cyanogen, the odour of which for any length of time is insupportable, the gas was drawn, by means of a common aspirator, through the liquid to be saturated, the flask which contained the gas allowing the entrance of air through a narrow tube drawn out to a fine point. By means of this simple apparatus, the current of the chloride was easily regulated, and I was not exposed for a single moment to the influence of this annoying compound.\*

On passing, in this manner, a current of chloride of cyanogen, prepared from cyanide of mercury, without further drying, into anhydrous aniline, chemical action is rendered at once perceptible by a rapid evolution of heat, the gas is absorbed with great avidity, the liquid assuming a brownish colour, and thickening gradually into a crystalline mass, the increasing consistency of which prevents the gas from passing freely. To complete the reaction, a gentle heat is now to be applied, sufficient to keep the compound in a state of fusion.

On cooling, the aniline is found converted into a solid transparent, slightly brownish, resinous substance, firmly adhering to the sides of the vessel. Towards the end of the operation, when the mass commences to become consistent, the absorption is exceedingly retarded, and the chloride of cyanogen passes into the aspirator. To avoid this loss, I have usually passed the gas through three wide test-tubes, half filled with aniline, and placed beside each other.

The viscid mass chiefly consists of the hydrochlorate of a new organic base, which, for reasons to be detailed hereafter, I propose to call *Melaniline*. The hydrochlorate is always mixed with another body, the quantity of which varies with the amount of moisture contained in the chloride of cyanogen. The formation of this second substance, of which I shall speak at another opportunity, prevents the use of the solution of chloride of cyanogen, which is obtained by acting with chlorine upon an aqueous solution of hydrocyanic acid. On treating aniline with this solution, the chief pro-

\* On pouring aniline directly into the bottles filled with chloride of cyanogen, a double compound is obtained, composed of the product newly formed and the chloride of mercury from the preparation. The purification of the new compound becoming thus more difficult, I was induced to relinquish this mode of procedure.

duct of the reaction is the second body above alluded to, whilst traces only of melaniline are formed.

*Preparation of melaniline.*—The crude product of the action of chloride of cyanogen on aniline, provided the treatment has been continued long enough, dissolves almost entirely in water, only a few brown drops remaining insoluble. The solution is considerably facilitated by boiling, and by the addition of a small quantity of hydrochloric acid. On adding ammonia, or better, a solution of potash, to the filtered liquid, a white viscid mass is separated, which solidifies after a few moments into a hard crystalline compound. If the treatment with chloride of cyanogen has been incomplete, the solidification takes place only very gradually, the separated alkaloid being mixed with undecomposed aniline.

In order to purify the crude melaniline, the precipitate is freed from chloride of potassium by washing with cold water, and recrystallized once or twice from a mixture of equal volumes of alcohol and water. The boiling solution deposits the base, on cooling, in white plates of perfect purity.

*Composition of melaniline*—The analysis of this base offered no difficulties, melaniline itself, as well as all its compounds, burning with great facility. The specimens of the base, its salts, and products of decomposition, were dried at 100° C.

When burnt with oxide of copper, the following numbers were obtained :

I.	0·2414 grm. melaniline gave			
	0·6500 " carbonic acid, and			
	0·1382 " water.			
II.	0·3423 " melaniline gave			
	0·9290 " carbonic acid, and			
	0·2013 " water.			
III.	0·2258 " melaniline gave			
	0·6104 " carbonic acid, and			
	0·1333 " water.			
IV.	0·2282 " melaniline gave			
	0·6180 " carbonic acid, and			
	0·1277 " water.			

These numbers lead to the following composition per cent. :

	I.	II.	III.	IV.
Carbon . . . . .	73·44	74·01	73·72	73·85
Hydrogen . . . . .	6·36	6·53	6·55	6·21

The nitrogen was determined according to the method of Bunsen; the following were the results obtained :

	Corrected volume of the moist gas	Temp. C.	Bar.
Level of mercury in the trough . . . . .	260·0 mm.		
Level of mercury in the tube	118·0	116·7	13·6° 733·7 mm.

Height of mercury . . . . 142·0

Dry volume of gas reduced } = 64·49  
to 0° C. and 1000 mm. bar.

After absorption of the carbonic acid :

	Corrected volume of dry nitrogen	Temp. C.	Bar.
Level of mercury in the trough . . . . .	261·0 mm.		
Level of mercury in the tube	16·4	14·2	13·3° 735·4 mm.

Height of mercury . . . . 244·6

Dry volume of nitrogen re-  
duced to 0° C. and 1000 } = 6·64  
mm. bar.

Ratio of carbon equivalents, and nitrogen equivalents :

$$64·49 - 6·64 : 6·64 = 100 : 11·48.$$

Calculating from the mean per centage of carbon found (73·75), this ratio leads to 19·75 per cent of nitrogen.

The above per centage composition, together with the analysis of various salts, lead to the following formula for melaniline :



as may be seen from the subjoined table.

	Theory.	Mean of experiments.
26 equivs. Carbon . . . .	156	73·93
13 " Hydrogen . . . .	13	6·16
3 " Nitrogen . . . .	42	19·91
1 " Melaniline . . . .	211	100·00
		99·91

This formula was controlled by numerous determinations of the atomic weight.

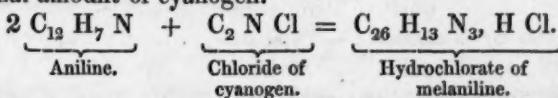
The analysis of a well-crystallized double salt of platinum gave as the mean of four nearly corresponding determinations, 23·48 per cent

of platinum. Five determinations of gold, in a similar double salt of gold yielded 35·714 per cent of gold.

Equivalent deduced from the platinum-salt . . . . .	214·02
Equivalent deduced from the gold-salt . . . . .	211·04
Mean . . . . .	212·53
Theoretical equivalent. . . . .	211·00

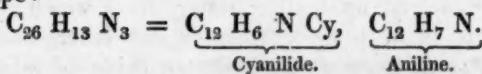
A more perfect coincidence could not be expected.

The formula given above for melaniline explains the mode of formation of this new body in a most satisfactory manner. It is obvious at the first glance, that melaniline is produced by the fusion of two aniline atoms, which have lost one equivalent of hydrogen in the form of hydrochloric acid, and have simultaneously assimilated a proportional amount of cyanogen.

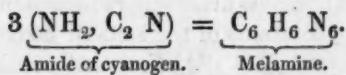


If the chloride of cyanogen is freed from the small quantity of moisture which it carries up from the bottles in which it has been prepared, by passing it through a chloride of calcium tube, we find, indeed, that the whole mass of aniline is converted into hydrochlorate of melaniline, according to the above equation. The crystals which are deposited at the commencement of the reaction, are hydrochlorate of aniline, and these are gradually converted into the corresponding melaniline salt.

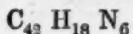
From the mode in which it is formed, the basic atom of melaniline may be regarded as an intimate combination of aniline with cyanide, whence the rational formula of the new compound assumes the following shape :



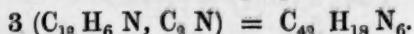
A corresponding ammonia-compound has not yet been observed, but it is at once evident that there exists a certain analogy between this new body and the melamine discovered by Professor Liebig. The latter alkaloid may be considered as a compound in which three equivalents of amide of cyanogen have been fused into one basic atom.



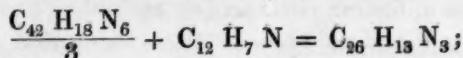
An aniline base, exactly corresponding to melamine, would have the composition



as will be apparent from the following equation :



In the new compound we have a third of the true aniline-melamine, associated with an additional equivalent of aniline :



a conjugated base is thus formed, which likewise saturates only *one* equivalent of acid.

The name *melaniline*, which I have adopted, should, therefore, be regarded as a convenient, but provisional term, in place of which another more rational one must be substituted, as soon as our views respecting the mode of combination of the elements in this compound have gained a more positive foundation.

*Properties of melaniline.*—This base, when pure, crystallizes in white, hard, pulverizable plates, which, if exposed to the air while damp, easily assume a slight red tinge.

The crystals are quite devoid of smell ; they have, however, a bitter taste (particularly when in alcoholic solution) which remains for some time on the palate. They fuse at about  $120^{\circ}$ — $130^{\circ}$  C. to a slightly coloured oil, which, on cooling, solidifies with a crystalline texture ; if, however, the temperature is raised to  $140^{\circ}$  or  $150^{\circ}$  C., decomposition ensues, colourless aniline distils over, and a transparent light brown amorphous mass remains in the retort. I shall return to this remarkable decomposition at another opportunity. The crystals of melaniline float on the surface of water ; but, when fused, the base sinks to the bottom.

Melaniline is only slightly soluble in cold water ; a somewhat larger quantity is dissolved by boiling water, from which, on cooling, it crystallizes in small plates. Alcohol and ether dissolve the base with facility, as do likewise the hydrated oxide of methyle, acetone, bisulphide of carbon, and fatty and ethereal oils. Melaniline crystallizes best from a boiling mixture of water and alcohol, in which the latter predominates ; on allowing the solution to cool gradually, the base is deposited in long white needles. Melaniline has scarcely any action on vegetable colours ; turmeric paper is not changed in the least by it, and only the most delicately reddened litmus paper is tinged slightly blue. The solutions of the salts of melaniline do not colour fir-wood ; chromic acid does not effect that peculiar change which it occasions in aniline salts. A solution of melaniline may be heated to ebullition with dilute chromic acid without a reduction of the acid occurring (only on continued boiling, the base is gradually attacked

and resolved into other compounds) ; nor does a solution of hypochlorite of lime produce the violet colour characteristic of aniline.

An aqueous solution of melaniline, in consequence of the slight solubility of this base in water, affords precipitates with very few reagents. Salts of oxide and sesquioxide of iron are not precipitated ; solution of sulphate of zinc is rendered slightly turbid ; sulphate of copper, nitrate of silver, and chloride of mercury, produce flocculent precipitates, which are double compounds of the base. Of these I have investigated only the silver precipitate. Bichloride of platinum and terchloride of gold produce beautiful double compounds with the hydrochlorate, to which I shall recur hereafter.

*Combinations of Melaniline.*—The base dissolves easily in all acids, with a slight evolution of heat, and forms with most of them nicely crystallizable, colourless or slightly reddish salts, which are capable of double decomposition.

The neutral salts of melaniline have no action on reddened litmus paper. They are exactly analogous in their constitution to the salts of ammonia. Their solutions, all of which possess an intensely bitter taste, are decomposed by ammonia, and more perfectly by potash or soda, the melaniline being separated as a dazzling white precipitate, which becomes crystalline almost immediately. The carbonates of the alkalies likewise precipitate the base, with evolution of carbonic acid.

With respect to its basic properties, melaniline is nearly allied to aniline ; an aniline salt cannot be decomposed by melaniline, nor has aniline any action on the salts of the other base.

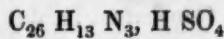
I have submitted several salts of melaniline to a closer examination, in order to obtain further proof of the correctness of the formula given above.

*Sulphate of melaniline.*—This salt crystallizes a short time after the solutions are mixed, in rhombic plates, which aggregate into star-like groups. The crystals are somewhat difficultly soluble in cold, more easily in boiling water. They likewise dissolve in alcohol and ether.

A determination of the sulphuric acid gave the following results :

0·3585 grm. sulphate of melaniline, dried at 100° C. gave 0·1572 grm. sulphate of barytes, corresponding to 18.42 per cent. of hydrated sulphuric acid.

Hence, the salt is a neutral sulphate, having the formula

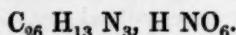


	Theory.	Experiment.
1 eq. Melaniline . . . . .	211	81·16
1 „ Hydrated sulphuric acid	49	18·84
1 „ Sulphate of melaniline	260	100·00

*Nitrate of melaniline.*—This compound is that which of all the salts of melaniline crystallizes with the greatest ease; it separates from a boiling aqueous solution on cooling, in needles, and indeed, so completely, that the mother-liquor gives but a very faint precipitate with ammonia or potash. I was thus frequently enabled, during the progress of this investigation, to apply nitric acid as a reagent for melaniline.

This salt is soluble in alcohol, but scarcely so in ether; it is stable in atmospheric air, but very soon acquires a red tint.

The analysis of this salt led to the formula



When burnt with oxide of copper, the following numbers were obtained:

0·2831 grm. nitrate of melaniline gave  
 0·5872 „ carbonic acid, and  
 0·1318 „ water.

	Theory.	Experiment.
26 eq. Carbon . . . . .	156	56·93
14 „ Hydrogen . . . . .	14	5·10
4 „ Nitrogen . . . . .	56	20·43
6 „ Oxygen . . . . .	48	17·54
1 eq. Nitrate of melaniline .	274	100·00

*Binoxalate of melaniline.*—This compound is exactly similar in outward appearance to the sulphate; it crystallizes when the base is supersaturated with oxalic acid. The crystals are difficultly soluble in water and in alcohol, when cold, but easily at the boiling temperature. They are nearly insoluble in ether. The salt, when heated, evolves equal volumes of carbonic oxide and carbonic acid, and aniline distils over, accompanied by the same pungent body which I had occasion to mention in my description of cyaniline. At the close of the operation, the neck of the retort becomes coated with long white needles, and a transparent residue remains, similar to that

obtained on heating melaniline. The analyses of this salt show it to be a binoxalate, as is indicated by its acid reaction.

- I. 0·5560 grm. binoxalate of melaniline, precipitated with ammonia and chloride of calcium, &c., yielded  
 0·1840 grm. carbonate of lime.  
 II. 0·491 „ of the salt gave  
 1·0866 „ carbonic acid, and  
 0·2302 „ water.

The formula,

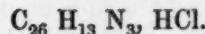


requires the following numbers:

	Theory.		Experiment I.
1 eq. Melaniline . . . . .	211	70·10	—
2 „ Hydrated oxalic acid . .	90	29·90	29·73
1 eq. Binoxalate of melaniline	301	100·00	
	Theory.		Experiment II.
30 eq. Carbon . . . . .	180	59·80	60·35
15 „ Hydrogen . . . . .	15	4·98	5·20
3 „ Nitrogen . . . . .	42	13·95	—
8 „ Oxygen . . . . .	64	21·27	—
1 eq. Binoxalate of melaniline	301	100·00	

*Phosphate of melaniline.*—This salt is very soluble, and crystallizes slowly. I have not analyzed it.

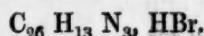
*Hydrochlorate of melaniline.*—This is the most soluble of all the melaniline salts. The solution of the base in hydrochloric acid does not crystallize by spontaneous evaporation in the open air. When kept over sulphuric acid, or in a water-bath, it dries up to a slightly coloured gummy mass, which only becomes crystalline very gradually. It is hence difficult to obtain this salt in a fit state for analysis. I endeavoured to determine its composition, by ascertaining the increase of weight produced by dissolving the base in hydrochloric acid, and desiccating. It appears, however, that the whole excess of acid cannot be removed in this manner. I obtained, in one experiment of this kind, 16 per cent of hydrochloric acid, instead of 14·74 per cent., which would correspond to the formula



*Hydrobromate of melaniline.*—This salt is likewise very soluble, less so, however, than the hydrochlorate, and may be obtained

without difficulty in fine stellated tufts of needles. It is, like the corresponding cyaniline salt, less soluble in concentrated hydrobromic acid than in water.

Its analysis led to the formula,



0·3494 grm. hydrobromate of melaniline gave

0·2252 „ bromide of silver.

	Theory.	Experiment.
1 eq. Melaniline . . . . .	211·00	72·70
1 „ Hydriodic acid . . . . .	79·26	27·30
1 „ Hydrobromate of melaniline	290·26	100·00

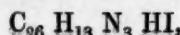
*Hydriodate of melaniline.*—A concentrated solution of hydriodic acid converts the base into a yellow oil, which falls to the bottom of the vessel, and solidifies after a time to a crystalline mass. This is soluble in boiling water, being again separated on cooling, in oily drops, which only gradually solidify. It is likewise soluble in alcohol. When in contact with air, it is rapidly decomposed, the hydriodic acid undergoing decomposition with separation of iodine.

The specimen employed in the following analysis had been superficially decomposed; hence the slight loss of iodine.

0·6727 grm. hydriodate of melaniline gave

0·4575 „ iodide of silver.

The formula :



requires :

	Theory.	Experiment.
1 eq. Melaniline . . . . .	211·00	62·36
1 „ Hydriodic acid . . . . .	127·36	37·64
1 „ Hydriodate of melaniline	338·36	100·00

*Hydrofluorate of melaniline.*—This salt is easily formed by dissolving melaniline in dilute hydrofluoric acid. It may be obtained in well formed crystals, which, however, possess always a reddish tint. It is pretty soluble in water, less so in alcohol.

*Bichloride of platinum and melaniline.*—Bichloride of platinum produces, in a solution of the hydrochlorate, a slightly crystalline, pale yellow precipitate. The filtrate deposits, after a time, regular orange-

yellow crystals. These, and the precipitate, have the same composition.

This platinum salt is slightly soluble in boiling water, the yellow crystals being also deposited on cooling. It is less soluble in alcohol, and insoluble in ether.

The analysis of specimens of different preparations, gave the following results :—

- I. 0·5585 grm. of platinum salt, burnt with chromate of lead gave
  - 0·7621 " " carbonic acid, and
  - 0·1836 " " water.
- II. 0·6875 " " platinum salt ignited with lime, dissolved in nitric acid and precipitated with nitrate of silver, gave 0·7085 grm. of chloride of silver.
- III. 0·3707 " " platinum-salt, yielded 0·0871 " " platinum.
- IV. 0·5030 " " platinum-salt, yielded 0·1187 " " platinum.
- V. 0·2670 " " platinum-salt, yielded 0·0623 " " platinum.

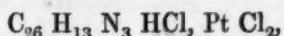
The following determination was made with the crystallized salt :

- VI. 0·3697 grm. of platinum-salt, yielded 0·087 " " platinum.

From these numbers, the following per centage composition is deduced :

	I.	II.	III.	IV.	V.	VI.
Carbon . . .	37·21	—	—	—	—	—
Hydrogen . . .	3·65	—	—	—	—	—
Chlorine . . .	—	25·49	—	—	—	—
Platinum . . .	—	—	23·49	23·59	23·83	23·53

The formula :



requires the following numbers :

	Theory.	Mean of experiment.
26 eq. Carbon . . . . .	156·00	37·39
14 " Hydrogen . . . . .	14·00	3·35
3 " Nitrogen . . . . .	42·00	10·09
3 " Chlorine . . . . .	106·50	25·52
1 " Platinum . . . . .	98·68	23·65
1 " Platinum-salt . . . . .	417·18	100·00

*Terchloride of gold and melaniline.*—On mixing a moderately concentrated solution of hydrochlorate of melaniline with terchloride of gold, the liquid immediately assumes a deep yellow colour, becoming turbid and opaque. In about half an hour, it again becomes clear, and is now filled with splendid gold-coloured needles. If the solution of the hydrochlorate is concentrated, terchloride of gold produces an abundant yellow precipitate. The salt is difficultly soluble in water, but more easily in alcohol, and is exceedingly soluble in ether. If the precipitate suspended in water is shaken with ether, a deep yellow ethereal solution of the salt is obtained floating on the colourless liquid. If this solution is allowed to evaporate spontaneously, it sinks to the bottom of the water, at a certain state of concentration, in the form of oily drops of a ruby colour, which solidify, after a time, in the form of beautiful four-sided prisms.

Its analysis gave the following numbers:

I.	0·6791 grm. of gold-salt, gave
	0·7125 " " carbonic acid, and
	0·1635 " " water.
II.	0·215 " " gold-salt, gave
	0·0765 " " gold.
III.	0·8259 " " gold-salt, gave
	0·2956 " " gold.

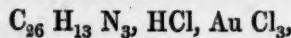
In the analyses II. and III. the salt was employed in the precipitated state; for the following determinations, the salt had been crystallized from ether;

IV.	0·2785 grm. of gold-salt, gave
	0·0995 " " gold.
V.	0·3374 " " gold-salt, gave
	0·1207 " " gold.
VI.	0·3663 " " gold-salt, gave
	0·1309 " " gold.

From these numbers, the following per centage composition is deduced:

	I.	II.	III.	IV.	V.	VI.
Carbon . . .	28·61	—	—	—	—	—
Hydrogen . . .	2·67	—	—	—	—	—
Gold . . . .	—	35·58	35·79	35·72	35·77	35·73

which lead to the formula:



as may be seen from the subjoined table :

	Theory.	Experiment.
26 eq. Carbon . . . . .	156.00	28.32
14 „ Hydrogen . . . . .	14.00	2.54
3 „ Nitrogen . . . . .	42.00	7.62
4 „ Chlorine . . . . .	142.00	25.81
1 „ Gold . . . . .	196.66	35.71
<b>1 „ Gold-salt . . . . .</b>	<b>550.66</b>	<b>100.00</b>

*Nitrate of silver and melaniline.*—An alcoholic solution of melaniline produces, with nitrate of silver, a white precipitate, which adheres firmly to the sides of the vessel in the form of a resinous matter. I collected this mass with a glass rod, and reduced it to a fine powder with alcohol, to remove any excess of melaniline; it was then washed with alcohol (I). On endeavouring to crystallize a portion from alcohol, it was decomposed with the separation of metallic silver. The same compound may be obtained in hard, rounded crystals, on mixing alcoholic solutions of melaniline and nitrate of silver. The liquid remains clear for some hours, it then slowly deposits the compound (II).

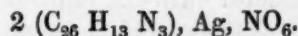
Both preparations burnt with the greatest difficulty.

- I. 0.2492 grm. of silver-salt, gave  
0.043 „ „ metallic silver.
- II. 0.320 „ „ silver-salt, gave  
0.057 „ „ metallic silver.

Which correspond to the following composition per cent :

	I.	II.
Silver . . . . .	17.41	17.81

The amount of silver found, corresponds approximately to the formula :



	Theory.	Mean of experiments.
2 eq. Melaniline. . . . .	422	72.28
1 „ Silver . . . . .	108	18.24
1 „ NO <sub>6</sub> . . . . .	62	10.47
<b>1 „ Silver-salt . . . . .</b>	<b>592</b>	<b>100.47</b>

I have not had time to confirm this somewhat uncommon composition by further experiments.

Chloride of mercury gives a white precipitate, in solutions of melaniline, which is easily soluble in a few drops of hydrochloric acid.

By spontaneous evaporation, this solution deposits long white needles.

*Metamorphoses of melaniline.*—The following pages contain a few observations respecting the transformations of melaniline when exposed to the action of various agents. These transformations, however, present so great a diversity, the descendants of melaniline ramify in so many directions, that these remarks must only be considered as a first contribution towards this part of the history of our compound. As soon as I find leisure, I hope to return to this subject.

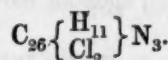
*Action of chlorine on melaniline—Dichloromelaniline.*—From the complete transformation of aniline, when under the influence of chlorine, a still more decided action might have been expected in the case of melaniline, this body being evidently a compound of a higher order. It appeared not improbable that this reaction might throw some light upon the real manner in which the elements are combined in melaniline. This expectation has remained as yet unfulfilled, the action of chlorine, as far, at least, as I have studied it, assuming merely the form of a simple process of substitution.

If a solution of hydrochlorate of melaniline is mixed with a large excess of chlorine water, the whole of the base is separated in the form of a resinous mass, which becomes hard after a time, but shews no signs of crystallization. The filtrate is no longer precipitated by potash. The resinous body is insoluble in water, but soluble in alcohol; it possesses neither basic nor acid properties. I have not analyzed it, but its general deportment characterizes it as a substitution-product, bearing a relation to melaniline, similar to that which trichloraniline bears to aniline.

On adding chlorine water, gradually and in small quantities, to a solution of hydrochlorate of melaniline, the liquid becomes turbid after each addition, but is rendered immediately clear by agitation. The point may be easily attained when the resinous mass, that separates, no longer dissolves on agitation. If the solution is now filtered and evaporated till a pellicle forms, it deposits, on cooling, stellated groups of white needles. If the evaporation has been carried too far, a yellowish oil separates, which becomes solid and exhibits a crystalline texture.

These crystals are the hydrochlorate of a chlorinated base, which I propose to call *dichloromelaniline*. They are easily soluble in ether, and tolerably so in alcohol, but dissolve with difficulty in water. Ammonia precipitates the base from the hydrochloric solution as a dazzling white flocculent substance, crystallizing from alcohol in hard plates. I have not analyzed either the hydrochlorate or the base, as I have carefully investigated the analogous bromine compounds.

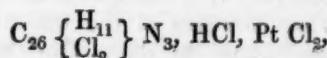
The analysis of the platinum-salt, however, which I subjoin, proves undoubtedly, that the body in question is dichloromelaniline :



*Bichloride of platinum and dichloromelaniline.*—The solution of the hydrochlorate gives, with bichloride of platinum, a fine orange-yellow precipitate, which is easily purified by washing with ether. The analysis of this compound gave the following results :

0·3435	grm. of platinum-salt, when burnt with chromate of lead,
	gave
0·4039	„ „ carbonic acid, and
0·0785	„ „ water.
0·1976	„ „ platinum-salt, yielded
0·0400	„ „ platinum.

The per centage composition deduced from these experiments leads to the formula :



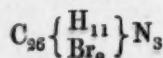
as may be seen from the following table :

	Theory.	Experiment.
26 eq. Carbon . . . .	156·00	32·08
12 „ Hydrogen . . . .	12·00	2·46
3 „ Nitrogen . . . .	42·00	8·63
5 „ Chlorine . . . .	177·50	36·54
1 „ Platinum . . . .	98·68	20·29
<hr/>		<hr/>
1 „ Bichloride of platinum and dichloromelaniline }	486·18	100·00

*Action of bromine on melaniline.*—The phenomena observed on treating a solution of the hydrochlorate of melaniline with bromine are very similar to those obtained with chlorine. The white crystals obtained on evaporating the solution are the hydrochlorate of a new brominated base.

*Dibromomelaniline.*—The solution of the salt just mentioned deposits, on the addition of ammonia, a white crystalline mass, which separates in white scales from boiling alcohol.

These crystals are *dibromomelaniline*.



as the following analysis proves :

0·3980 grm. of the base, when burnt with chromate of lead, gave  
 0·6180 „ carbonic acid, and  
 0·1000 „ water.

		Theory.	Experiment.
26 equivs. Carbon . . .	156·00	42·67	42·37
11 " Hydrogen . . .	11·00	3·00	2·80*
3 " Nitrogen. . .	42·00	11·49	—
2 " Bromine. . .	156·52	42·84	—
 1 " Dibromomelaniline	365·52	100·00	

Dibromomelaniline is nearly insoluble in water; it is dissolved, however, easily by alcohol and ether. These solutions possess a very bitter taste. When heated, this body exhibits a deportment similar to that of melaniline. On raising the temperature above the fusing point of the base, a colourless vapour is evolved, which condenses in the neck of the retort into a colourless liquid, solidifying after some time to a slightly yellow, crystalline mass. These crystals are pure *bromaniline*. There remains in the retort a resinous mass, of precisely the same appearance as the residue of the distillation of melaniline. This decomposition offers some interest, pointing out, as it does, a method of obtaining *bromaniline*, and, of course, also *chloraniline*, directly from aniline; substances which could hitherto be prepared only by the action of alkalies on chlorinated and brominated isatine.

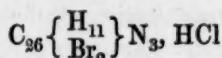
I have analyzed only the hydrochlorate and the platinum compound of dibromomelaniline.

*Hydrochlorate of dibromomelaniline*.—This substance crystallizes in white stellated needles of a silky lustre, which, when deposited from a slowly-cooling solution, sometimes attain the length of a centimeter. They are but slightly soluble in water, and fuse, when boiled in an insufficient quantity, into a yellow oil, which solidifies, on cooling, into a crystalline mass.

The analysis gave the following results :

0·2866 grm. hydrochlorate of dibromomelaniline gave  
 0·1038 „ chloride of silver,  
 which corresponds to 9·2 per cent of hydrochloric acid.

The formula



\* The deficiency of hydrogen was occasioned by the moistening of the cork, which had been kept too cool during the combustion.

requires the following numbers :

	Theory.	Experiment.	
1 equiv. dibromomelaniline . . . . .	365.52	90.92	—
1 " hydrochloric acid . . . . .	36.50	9.08	9.21
1 " hydrochlorate of dibromomelaniline	402.02	100.00	

*Bichloride of platinum and dibromomelaniline.*—A boiling solution of the hydrochlorate gives, with a concentrated solution of bichloride of platinum, an orange-yellow precipitate, which, on cooling, is converted into splendid scales of a golden lustre. This salt is insoluble in water, scarcely soluble in ether, and somewhat more soluble in alcohol.

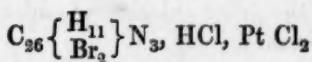
The analysis yielded the following results :

I. 0.3740 grm. of platinum-salt gave	
0.3768 " " carbonic acid	
0.0781 " " water.	
II. 0.2220 " " platinum-salt yielded	
0.0330 " " platinum,	

which correspond to the following per centage composition :

	I.	II.
Carbon . . . . .	27.45	—
Hydrogen . . . . .	2.32	—
Platinum . . . . .	—	17.11

The formula



requires the following numbers :

	Theory.	Experiment.
26 equivs. Carbon . . . . .	156.00	27.28
12 " Hydrogen . . . . .	12.00	2.09
3 " Nitrogen . . . . .	42.00	7.38
2 " Bromine . . . . .	156.52	27.37
3 " Chlorine . . . . .	106.50	18.62
1 " Platinum . . . . .	98.68	17.26
1 " Bichloride of platinum and dibromomelaniline	571.70	100.00

I have tried to arrest the action of bromine, so as to obtain a compound containing only one equivalent of bromine, by treating a solution of hydrochlorate of melaniline with small quantities of

bromine, and adding the ammonia long before any lasting precipitate produced by bromine appears; in this manner, a precipitate is obtained containing a smaller amount of bromine.

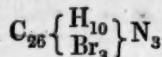
I have converted several of these precipitates into platinum salts; these salts left, on ignition, slightly varying quantities of platinum, generally shewing a close approximation to the per centage of a monobromomelaniline platinum-salt. I do not, however, feel justified in announcing the existence of such a compound, the products in question not presenting a sufficiently definite character to warrant such affirmation.

These precipitates may just as well have been mixtures of undecomposed melaniline and dibromomelaniline; melaniline being formed by the union of two atoms of aniline, it remains doubtful whether the action of bromine can possibly be confined to one equivalent.

By treating melaniline with an excess of bromine, the substitution-products become less and less basic, until at last a perfectly indifferent resinous body is formed, which I have not analyzed. It is, perhaps, a compound corresponding to tribromaniline, containing six equivalents of bromine. Between this last term of the series and dibromomelaniline, we may assume the existence of several intermediate compounds. The rapidly decreasing property of crystallization in these substances, however, renders a perfect separation almost impossible.

I may still mention the following experiment. A solution of hydrochlorate of melaniline, treated with bromine until it had deposited crystals of the hydrochlorate of dibromomelaniline, was again exposed to the action of bromine. On evaporation, transparent yellow, oily drops were separated, solidifying only after some time to a slightly crystalline mass, the alcoholic solution of which gave, with bichloride of platinum, a resinous precipitate, which likewise became slowly crystalline. In order to purify this, it was dissolved in a large quantity of boiling alcohol, from which it separated, on cooling, in crystalline crusts.

According to the platinum determination, these crystals would be the platinum salt of a tribromomelaniline:



0.8824 grm. of platinum-salt left

0.0574 " " platinum,

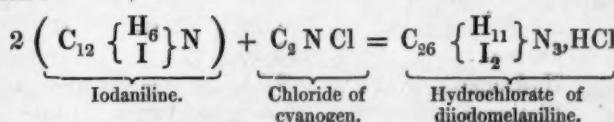
which gives 15.00 as the per centage of platinum. The calculated per centage is 15.25.

The experimental evidence, however, of the existence of such a compound is likewise insufficient.

*Action of iodine on melaniline.*—I did not succeed in preparing diiodinated melaniline by the action of iodine on melaniline. A solution of the hydrochlorate of this base, when treated with an excess of iodine, deposits a black, sticky mass, scarcely a trace of the base remaining in solution; if the hydrochlorate is gradually mixed with small quantities of an alcoholic solution of iodine, the same precipitate is formed, but the base remaining in solution is unchanged melaniline.

Diiodomelaniline may, however, be easily obtained by treating an etherial solution of iodaniline with chloride of cyanogen. On passing this gas into the solution, a crystalline precipitate is soon deposited, which is hydrochlorate of iodaniline; by continuing this treatment, these crystals again disappear, and the whole is gradually converted into a resinous mass of hydrochlorate of diiodomelaniline, which slowly becomes crystalline.

The formation of this compound is represented by the following equation :



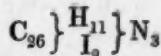
Hydrochlorate of diiodomelaniline resembles very much the corresponding salts of the chlorinated and brominated bases. It is very little soluble in water, and separates from the boiling solution in oily drops, which are very slowly converted into beautiful white tufts: I have not examined this salt further.

Diiodomelaniline is separated by ammonia, or better, by potash, from the preceding hydrochlorate as a white precipitate, which crystallizes from alcohol, though less perfectly than the chlorine and bromine bases, which it resembles in every other respect.

The combustion of this compound gave a slight excess of hydrogen, most probably from a small quantity of iodine, which might have been carried over into the chloride of calcium tube.

0·8255 grm. diiodomelaniline gave  
0·4046 " carbonic acid, and  
0·0795 " water.

The formula



requires the following numbers :

	Theory.	Experiment.
26 equivs. Carbon . . . .	156·00	33·78
11 " Hydrogen . . . .	11·00	2·37
2 " Iodine . . . .	252·72	54·76
3 " Nitrogen . . . .	42·00	9·09
1 " Diiodomelaniline .	461·72	100·00

*Bichloride of platinum and diiodomelaniline.*—To control the above analysis, I prepared the platinum-salt of the iodine base. It resembles the platinum compounds of the chlorine and bromine bases, although it is less crystalline.

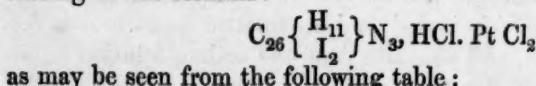
The analysis of this salt gave the following numbers :

I. 0·2580 grm. of the platinum-salt gave		
0·2195 " " carbonic acid		
0·0490 " " water.		
II. 0·1310 " " platinum-salt left		
0·0192 " " platinum.		
III. 0·2315 " " platinum-salt gave		
0·0340 " " platinum.		

Per centage composition :

	I.	II.	III.
Carbon . . . . .	23·20	—	—
Hydrogen . . . . .	2·11	—	—
Platinum . . . . .	—	14·66	14·68

leading to the formula :



as may be seen from the following table :

	Theory	Experiment
26 equivs. of Carbon . . . . .	156	23·35
12 " " Hydrogen . . . . .	12	1·79
3 " " Nitrogen. . . . .	42	6·28
2 " " Iodine . . . . .	252·72	37·86
3 " " Chlorine. . . . .	106·50	15·95
1 " " Platinum. . . . .	98·68	14·77
1 " " Bichloride of platinum and Diiodomelaniline	667·90	100·00

*Action of nitric acid on melaniline.*—Common nitric acid dissolves melaniline with a considerable evolution of heat ; the solution solidifies after a few moments into a hard crystalline mass of the nitrate of melaniline : if a more concentrated, or a large excess of the common acid be employed, or if the solution is heated to ebullition, a most

violent reaction ensues, which cannot be kept under control, and the base is converted into a variety of products.

I have not been able to moderate the action of nitric acid in such a manner as to obtain a substitution-product analogous to the preceding chlorine and bromine compounds.

The action of fuming nitric acid on melaniline is so powerful, that, if equal parts of acid and base are mixed, an explosion takes place, the melaniline being entirely decomposed with the evolution of a column of black smoke. By gradual treatment with fuming acid, melaniline, according to the time the action lasts, is converted, either into a magnificent new base, crystallizing in short prisms of an orange-yellow colour and violet iridescence; or into brownish-yellow crystals of a new acid, which forms scarlet salts with alkalies. In the commencement, I mistook the base produced in this reaction for dinitromelaniline; a more minute investigation soon shewed, however, that it bears a very different relation to melaniline from that of a simple substitution-product.

For this reason, I refrain from following the action of nitric acid on melaniline any further. The nitro-base, corresponding to dinitromelaniline, is, however, easily formed, as was to be expected, by the action of chloride of cyanogen on nitraniline.

*Dinitromelaniline.*—The manner in which chloride of cyanogen is permitted to act on nitraniline, is by no means a matter of indifference; the simplest method appeared to be, to pass the gas through the fused base. Dinitromelaniline is, indeed, formed in this process: a large quantity of the nitraniline, however, seems to undergo, in this case, another decomposition. An aqueous solution of nitraniline undergoes a peculiar decomposition with chloride of cyanogen, which I intend to investigate more fully at a future period; an alcoholic solution is very slowly attacked. I found it most advantageous to employ an ethereal solution; on passing a current of chloride of cyanogen through an ethereal solution of nitraniline, until nearly the whole of the ether has been evaporated into the surrounding air, a residue is obtained, which contains two new bases, mixed with more or less of unchanged nitraniline. This residue, when heated with an insufficient quantity of water, fuses into a brown oil, which dissolves, however, almost completely in a considerable amount of boiling water.

This solution deposits yellowish needles on cooling, which we will only mention for the present. The colourless mother-liquor of this body contains the hydrochlorate of dinitromelaniline, which separates on the addition of ammonia, in the form of a bright sulphur-yellow precipitate, rapidly becoming crystalline.

	Theory.	Experiment.
26 equivs. Carbon . . . .	156·00	33·78
11 , " Hydrogen . . . .	11·00	2·37
2 , " Iodine . . . .	252·72	54·76
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	—————	—————
1 , " Diiodomelaniline .	461·72	100·00

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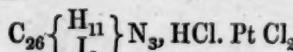
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	0·0192 , " , platinum.
III.	0·2315 , " , platinum-salt gave
	0·0340 , " , platinum.

Per centage composition :

	I.	II.	III.
Carbon . . . . .	23·20	—	—
Hydrogen . . . . .	2·11	—	—
Platinum . . . . .	—	14·66	14·68

leading to the formula :



as may be seen from the following table :

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For this reason, I refrain from following the action of nitric acid on melaniline any further. The nitro-base, corresponding to dinitromelaniline, is, however, easily formed, as was to be expected, by the action of chloride of cyanogen on nitraniline.

*Dinitromelaniline.*—The manner in which chloride of cyanogen is permitted to act on nitraniline, is by no means a matter of indifference; the simplest method appeared to be, to pass the gas through the fused base. Dinitromelaniline is, indeed, formed in this process: a large quantity of the nitraniline, however, seems to undergo, in this case, another decomposition. An aqueous solution of nitraniline undergoes a peculiar decomposition with chloride of cyanogen, which I intend to investigate more fully at a future period; an alcoholic solution is very slowly attacked. I found it most advantageous to employ an ethereal solution; on passing a current of chloride of cyanogen through an ethereal solution of nitraniline, until nearly the whole of the ether has been evaporated into the surrounding air, a residue is obtained, which contains two new bases, mixed with more or less of unchanged nitraniline. This residue, when heated with an insufficient quantity of water, fuses into a brown oil, which dissolves, however, almost completely in a considerable amount of boiling water.

This solution deposits yellowish needles on cooling, which we will only mention for the present. The colourless mother-liquor of this body contains the hydrochlorate of dinitromelaniline, which separates on the addition of ammonia, in the form of a bright sulphur-yellow precipitate, rapidly becoming crystalline.

These crystals may possibly still contain some nitraniline which has escaped decomposition ; it may be easily separated by treatment with boiling water, in which the new product is perfectly insoluble.

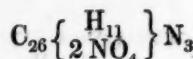
The analysis of the base itself, as well as of the hydrochlorate and of the platinum salt, leaves not the slightest doubt respecting the nature of this compound.

0·2393 grm. of the substance gave  
0·4538 " " carbonic acid, and  
0·0854 " " water.

The composition per cent is therefore :

Carbon . . .	51·71
Hydrogen . . .	3·96

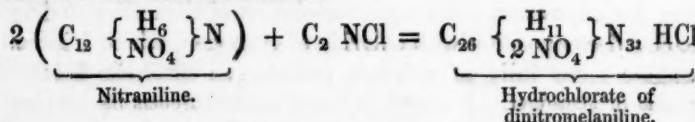
leading to the formula



which requires the following numbers :

	Theory.	Experiment.
26 equivs. of Carbon . . .	156	51·82
11 " " Hydrogen . . .	11	3·65
5 " " Nitrogen . . .	70	23·25
8 " " Oxygen . . .	64	21·28
<hr/>		
1 equiv. " Dinitromelaniline	301	100.00

The formation of this compound is perfectly analogous to that of melaniline and diiodomelaniline.



This new nitro-base, when precipitated from the hydrochlorate by ammonia or potash, appears as a scaly crystalline mass. It is at once distinguished from nitraniline by its brighter colour. It is difficultly soluble in alcohol, and still less soluble in ether. From the alcoholic solutions it is precipitated by water in the form of a splendid crystalline mass, possessing the lustre of metallic gold. Dinitromelaniline is unquestionably the most beautiful product of the whole series. The crystals which have been precipitated from an alcoholic solution by water appear under the microscope as short, flat needles ; crystals of the same shape, but much larger, may be obtained by allowing an ethereal solution of the base to evaporate spontaneously in narrow vessels.

The solutions of the base in alcohol and ether possess a deep yellow colour.

Dinitromelaniline is not volatile without decomposition. When heated, it undergoes a change similar to that of melaniline ; a yellow vapour is evolved, condensing on the cooler parts of the retort into brown, oily drops, which gradually become crystalline, whilst a brown, resinous substance remains in the retort.

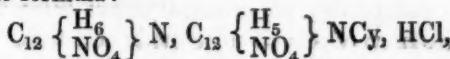
Dinitromelaniline forms, with most acids, well crystallizable salts, which in the solid state, as well as in solution, are perfectly colourless. I have analysed only two of them.

*Hydrochlorate of dinitromelaniline.* This salt crystallizes in flattened needles or plates of considerable lustre, and which are rather difficultly soluble, whilst the corresponding salt of nitraniline dissolves with the greatest facility.

0·2893 grms. of substance gave :

0·1230 " " chloride of silver.

Equivalent to 10·82 per cent of hydrochloric acid, which corresponds closely with the formula :



as is shown by the following table :

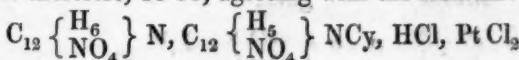
	Theory.	Experiment.
26 equv. of Carbon . . . . .	156·00	46·22
11 " " Hydrogen . . . . .	11·00	3·26
5 " " Nitrogen . . . . .	70·00	20·74
8 " " Oxygen . . . . .	64·00	18·97
1 " " Hydrochloric acid	36·50	10·81
1 " " Hydrochlorate of dinitromelaniline . . . . .	337·50	100·00

*Bichloride of platinum and dinitromelaniline.*—The solution of the preceding salt gives a yellow crystalline precipitate with bichloride of platinum, which is insoluble in water and alcohol, and only slightly soluble in ether. The platinum salt of nitraniline is very soluble in water. The platinum salt of dinitromelaniline, when heated, is decomposed with a slight deflagration : in determining the platinum, it was, therefore, necessary to ignite only a small quantity at a time in a covered platinum crucible. A determination of this kind gave the following results :

0·097 grm. of the salt, gave

0·019 " " platinum,

In 100 parts therefore, 19·58, agreeing with the formula :



x 2

as may be seen by the following table :

	Theory.	Found.
26 equivs. of Carbon . . .	156.00	30.76
13 " " Hydrogen . . .	12.00	2.38
5 " " Nitrogen . . .	70.00	13.60
8 " " Oxygen . . .	64.00	12.62
3 " " Chlorine . . .	106.50	21.19
1 " " Platinum . . .	98.68	19.45
1 " " Bichloride of platinum and dinitromelaniline	507.18	19.58
	100.00	

Of the other salts of dinitromelaniline, I have prepared only the nitrate, sulphate, and oxalate. The nitrate is difficultly soluble, like the corresponding salt of nitraniline, and crystallizes in indistinct needles. The sulphate and oxalate dissolve very readily in water, the former being deposited in crystals, the latter in granular tufts.

*Action of cyanogen on melaniline.*—The peculiar comportment of cyanogen with aniline and the analogous bases, with which I had become acquainted in former experiments, induced me to act with the same gas on melaniline; my principal object being to gain by this means another instance of this peculiar mode of action.

A cold saturated alcoholic solution of melaniline absorbs a very large quantity of cyanogen gas; the saturated liquid, when kept in a corked bottle, soon deposits yellowish crystalline crosses, of a satin lustre; and, after the lapse of a few hours, the whole solution has solidified to a soft crystalline mass: the odour of the cyanogen has now disappeared, whilst that of prussic acid is perceptible.

Dicyanomelaniline, the new substance, is insoluble in water; it dissolves, however, rather easily in boiling alcohol. In order to purify it, the brown mother-liquor is drained from the crystals, which are washed with cold alcohol. Two or three crystallizations from the same solvent (boiling) render the substance perfectly pure.

For the following analyses, specimens of different preparations were employed:

- I. 0.4051 grm. of substance, gave  
1.0200 " " of carbonic acid, and  
0.1980 " " water.
- II. 0.2544 " " substance, gave  
0.6411 " " carbonic acid, and  
0.1180 " " water.
- III. 0.3309 " " substance, gave  
0.8252 " " carbonic acid, and  
0.1525 " " water.
- IV. 0.2760 " " substance, gave  
0.6880 " " carbonic acid, and  
0.1200 " " water.

In 100 parts :

	I.	II.	III.	IV.
Carbon . . .	68·67	68·72	68·01	67·98
Hydrogen . . .	5·29	5·15	5·12	4·83

which leads to the formula :

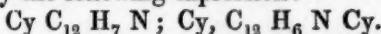


as may be seen from the following table:

	Theory.	Found.
30 equivs. of Carbon . . .	180	68·44
13 " " Hydrogen . . .	13	4·94
5 " " Nitrogen . . .	70	26·62
1 " " Dicyanomelaniline	263	100·00

Dicyanomelaniline (which name I propose for the new substance) is simply melaniline which has united with two equivalents of cyanogen; its formation is perfectly analogous to that of cyaniline. The assimilation of two equivalents of cyanogen is remarkable, although perfectly in accordance with the nature of melaniline.

It appears that both the aniline atoms (the intimate combination of which constitute melaniline,) still exhibit the same comportment with cyanogen as when in the isolated state, and if it be permitted to express an opinion respecting the probable arrangement of the elements by a formula, the constitution of dicyanomelaniline may be represented by the following expression :



Dicyanomelaniline, when pure, forms slightly yellowish needles; the colour seems to be peculiar to the compound, it cannot be separated by repeated treatment with animal charcoal. Like the other melaniline products, it is not volatile without decomposition; when heated, aniline and cyanide of ammonium are disengaged, while a resinous body remains in the retort, which chars at a higher temperature.

In dicyanomelaniline, the basic properties of melaniline are still perceptible: they appear, however, less prominent than in the descendants of substitution.

The cyanogen base dissolves with great facility in dilute acids in the cold; on adding ammonia to the acid solution, a few moments after it has been made, a white precipitate is thrown down, consisting of unaltered dicyanomelaniline. I have, however, vainly tried to prepare salts of this base.

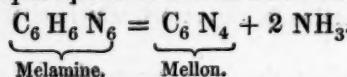
When describing the compounds of cyaniline, I mentioned that this base cannot remain in acid solutions, without soon undergoing

complete decomposition. The same comportment was exhibited in a far more decided manner with dicyanomelaniline. The clear solution of this base in hydrochloric acid deposits, after a few minutes, a yellow, slightly crystalline powder, which is by no means a hydrochlorate: the same metamorphosis ensues instantaneously on ebullition.

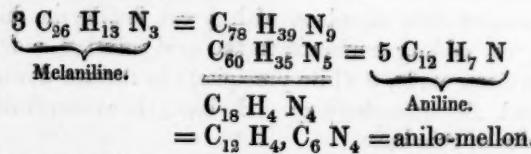
If a boiling alcoholic solution of dicyanomelaniline is mixed with an excess of hydrochloric acid, the liquid assumes a perfectly yellow colour, and, on cooling, beautiful white needles of another new body are deposited. In both cases the mother-liquor contains large quantities of ammonia.

For a more complete developement of these peculiar decompositions, a few data are still wanting at this moment, for which reason I refrain, at present, from any further details. I intend to return to this subject as soon as I shall have placed before the Society a description of the phenomena attending the decomposition of cyaniline, which, although simpler, present a certain degree of analogy with the above-mentioned changes. But I may mention now, that the products arising from the decomposition of dicyanomelaniline belong to the most remarkable substances which have been brought to light by this investigation. The comportment of melaniline, with other reagents, I have as yet only studied *en passant*. To complete this enumeration, a great number of experiments have to be performed; the behaviour, especially, which melaniline and its descendants exhibit under the influence of heat, requires a very close investigation. I have frequently alluded to this decomposition, with the study of which I am now engaged.

It is not unlikely that the residue in the retort is the mellon of the aniline series. If we recollect that melamine, when exposed to dry distillation, is split up into ammonia and mellon:

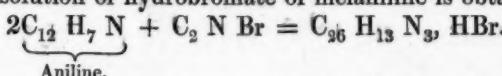


The idea naturally suggests itself, that an analogous decomposition takes place with melaniline:



These, however, are speculations unsupported as yet by experiment.

*Action of bromide of cyanogen on aniline.*—I have ascertained by experiment, that in this reaction exactly the same products are formed as with the chloride. The reaction proceeds only more slowly, owing to the inferior affinity of bromine for hydrogen. On treating with water, the crude product of the action of Serullas' bromide (prepared by the action of bromine on moistened cyanide of mercury), a solution of hydrobromate of melaniline is obtained:



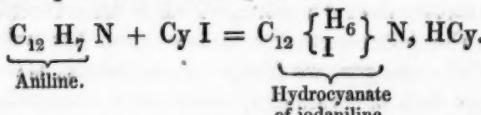
After precipitating the base from this solution by potash, the mother-liquor deposits, on evaporation, the same indifferent body, which I have mentioned when speaking of the action of the chloride. Although the properties of the base obtained by means of bromide of cyanogen did not admit of any doubt regarding its identity with melaniline, I have, nevertheless, made a determination of platinum:

Platinum-salt employed . . . . .	0·3316
Platinum obtained . . . . .	0·0786

which corresponds to the following composition per cent.:

Percentage of platinum in }	Theory.	Experiment.
the melaniline double salt } . . . . .	23·65	23·70

*Action of iodide of cyanogen on aniline.*—I have repeatedly treated aniline with iodide of cyanogen, which may be easily procured in any quantity by Liebig's process, viz., by dissolving iodine in a solution of crude cyanide of potassium. Iodine of cyanogen, however, is not capable of converting aniline into melaniline. In all my experiments, iodaniline only was formed, together with hydrocyanic acid, and a brown iodinated product of decomposition:



For the determination of platinum, No. II, mentioned in my paper on iodaniline,\* the base had been prepared by the action of iodide of cyanogen on aniline.

The following is a synoptical table of the members of the melaniline group which have as yet been studied:

Melaniline . . . . .	$C_{12}H_7N, C_{12}H_6N\text{Cy}$
Sulphate of melaniline . . .	$C_{12}H_7N, C_{12}H_6N\text{Cy}, H\text{SO}_4$
Nitrate of melaniline . . .	$C_{12}H_7N, C_{12}H_6N\text{Cy}, H\text{NO}_6$

\* Journal of the Chemical Society, vol. 1, 278.

Binoxalate of melaniline .	$C_{12}H_7N, C_{12}H_6N\text{Cy}, 2(HC_2O_4)$
Hydrochlorate of melaniline	$C_{12}H_7N, C_{12}H_6N\text{Cy}, HCl$
Hydrobromate of melaniline	$C_{12}H_7N, C_{12}H_6N\text{Cy}, HBr$
Hydriodate of melaniline .	$C_{12}H_7N, C_{12}H_6N\text{Cy}, HI$
Platinum-salt . . . . .	$C_{12}H_7N, C_{12}H_6N\text{Cy}, HCl, PtCl_2$
Gold-salt . . . . .	$C_{12}H_7N, C_{12}H_6N\text{Cy}, HCl, AuCl_3$
Silver-salt . . . . .	$2(C_{12}H_7N, C_{12}H_6N\text{Cy}), AgNO_6$
Dichloromelaniline .	$C_{12}\left\{\begin{matrix} H_6 \\ Cl \end{matrix}\right\}N, C_{12}\left\{\begin{matrix} H_5 \\ Cl \end{matrix}\right\}N, Cy$
Platinum-salt . . .	$C_{12}\left\{\begin{matrix} H_6 \\ Cl \end{matrix}\right\}N, C_{12}\left\{\begin{matrix} H_5 \\ Cl \end{matrix}\right\}N, Cy, HCl, PtCl_2$
Dibromomelaniline .	$C_{12}\left\{\begin{matrix} H_6 \\ Br \end{matrix}\right\}N, C_{12}\left\{\begin{matrix} H_5 \\ Br \end{matrix}\right\}N, Cy$
Hydrochlorate of } dibromomelaniline }	$C_{12}\left\{\begin{matrix} H_6 \\ Br \end{matrix}\right\}N, C_{12}\left\{\begin{matrix} H_5 \\ Br \end{matrix}\right\}N, Cy, HCl$
Platinum-salt . . .	$C_{12}\left\{\begin{matrix} H_6 \\ Br \end{matrix}\right\}N, C_{12}\left\{\begin{matrix} H_5 \\ Br \end{matrix}\right\}N, Cy, HCl, PtCl_2$
Diiodomelaniline .	$C_{12}\left\{\begin{matrix} H_6 \\ I \end{matrix}\right\}N, C_{12}\left\{\begin{matrix} H_5 \\ I \end{matrix}\right\}N, Cy$
Platinum-salt . . .	$C_{12}\left\{\begin{matrix} H_6 \\ I \end{matrix}\right\}N, C_{12}\left\{\begin{matrix} H_5 \\ I \end{matrix}\right\}N, Cy, HCl, PtCl_2$
Dinitromelaniline .	$C_{12}\left\{\begin{matrix} H_6 \\ NO_4 \end{matrix}\right\}N, C_{12}\left\{\begin{matrix} H_5 \\ NO_4 \end{matrix}\right\}N, Cy$
Hydrochlorate of } dinitromelaniline }	$C_{12}\left\{\begin{matrix} H_6 \\ NO_4 \end{matrix}\right\}N, C_{12}\left\{\begin{matrix} H_5 \\ NO_4 \end{matrix}\right\}N, Cy, HCl$
Platinum-salt . . .	$C_{12}\left\{\begin{matrix} H_6 \\ NO_4 \end{matrix}\right\}N, C_{12}\left\{\begin{matrix} H_5 \\ NO_4 \end{matrix}\right\}N, Cy, HCl, PtCl_2$
Dicyanomelaniline .	$C_{12}H_7N, C_{12}H_6N, Cy\left\{\begin{matrix} Cy \\ Cy \end{matrix}\right\}$

Melaniline is a conjugated base, of a similar, although more complicated constitution than cyaniline, which I have recently described. But while in the latter case, the aniline atom has only assimilated an equivalent of cyanogen, we find it in the former, associated with a complex compound of cyanogen, viz., with cyanilide. And this capability, which we observe in aniline, of combining with other substances without losing its basic properties, has by no means reached its limits in melaniline; in dicyanomelaniline, we see two new equivalents of cyanogen enter into the compound, and some preliminary experiments appear to indicate that this accumulation round the original atom may be carried still farther.

Facts, like these, deserve particular attention, containing, as they do, new confirmations of a general view of the organic bases which is daily gaining ground.

At a very early period, as far back as 1837, Berzelius, on the

ground of Liebig's researches, expressed the opinion, that the natural alkaloids, which at that period engrossed the undivided attention of chemists, were peculiar ammonia-compounds—conjugated compounds, in which the chemical character of ammonia, modified indeed by its conjunct, was still perceptible.

This view, which was principally founded on the remarkable analogy of the ammonia-salts and the salts of the alkaloids, met by no means with general approbation when first started; but it has been retained and carried out by Berzelius, with the perseverance and ratiocination which are peculiar to that great chemist. And it cannot be denied that since that period, science has acquired a great number of facts which powerfully support his opinion.

Organic chemistry has been enriched by a long and daily increasing series of artificial bases, formed in a variety of processes, many of which products we see generated by the direct action of ammonia on other compounds; chloride of platinum, when acted on by ammonia, gives rise to the various bases of Gros's and Reiset's salts; the ammonia-compound of cyanic acid, urea, is endowed with all the properties of the natural alkaloids. The ethereal oil of mustard, on combining with ammonia, is converted into thiosinnamine (Rhodalline, Berzelius) a weak organic base; and it is not unlikely that thiadline, the remarkable basic compound which Liebig and Wöhler\* obtained but lately by the action of hydrosulphuric acid on aldehydite of ammonia, must be considered as the ammonia compound of garlic oil. In a similar manner the bases, furfurine and picramine (amarine, benzoline), are formed by the action of ammonia on furfurole, or oil of bitter almonds. And here we observe the remarkable phenomenon, that the direct products of this action, viz., furfureamide and hydrobenzamide, are merely neutral substances, which, as the beautiful investigation of Professor Fownes has taught us, are converted only by the action of caustic alkalies into basic bodies, possessing exactly the same composition, but perfectly different physical properties. Hence it appears, that in furfureamide and hydrobenzamide, nitrogen is no longer contained in the form of ammonia. From the transition of these indifferent substances into bases, under the influence of reagents, giving rise in so many cases to the formation of ammonia; does it not become exceedingly probable, that in this case, part of the nitrogen has been re-converted into ammonia, which, uniting with the remaining elements, has impressed its character on the whole compound?

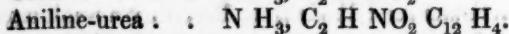
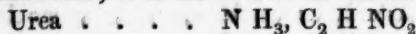
\* Mem. of the Chem. Soc.

It is scarcely to be doubted that the natural alkaloids, which we separate from plants, are formed in a similar manner. All the juices of plants contain more or less ammonia, by the action of which on the acids, on the indifferent principles, or on the ethereal oils, likewise contained in these juices, the generation of so numerous a class of bodies like the organic alkaloids, may be explained without difficulty.

Another series of researches has pointed out the close analogy between ammonia and the organic bases in a still more striking manner. Several years ago, I observed, that by the action of cyanic acid on aniline, a compound was produced, which from its properties, cannot be considered as cyanate of aniline, although it has exactly the composition of that salt.

The caustic alkalies, in the cold at least, evolve no aniline from this compound; mineral acids disengage neither cyanic acid nor its products of decomposition, a deportment which is sufficient to distinguish this compound from cyanate of aniline.

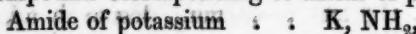
This body evidently bears to aniline the same relation which urea bears to ammonia; it is the urea of the aniline series:



Instances of a similar kind were soon found in abundance.

The deportment of ammonia with the metals of the alkalies, shews that one equivalent of hydrogen in this body is in a peculiar state of mobility, which admits of its easy elimination and replacement by other substances, a class of compounds, being thus produced, which we designate by the name of amides.

Exactly the same phenomenon is observed with aniline. On introducing potassium into anhydrous aniline, I observed \* a copious evolution of hydrogen, the base being converted into a viscid mass, capable of being decomposed by water, which was evidently the aniline compound corresponding to amide of potassium.



The dry distillation of ammoniacal salts has elicited a series of compounds, which can likewise be reproduced with the organic bases. Under the influence of temperatures of different intensities, neutral salts of oxide of ammonium lose either two or four equivalents of water; we obtain, in the first case, amides; in the second case, the class of substances which are at present designated by the name of nitryles.

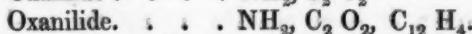
\* Liebig's Annalen, LVII.

Acid ammonia-salts, when distilled, exhibit exactly the same phenomenon ; they are converted by the elimination of two equivalents of water into amidogen acids ; by the abstraction of four equivalents, into imidogen compounds.

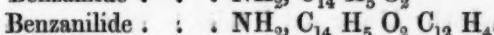
For all these classes, numerous and well-characterized representatives are known. Dumas' *oxamide*, and *benzamide*, discovered by Liebig and Wöhler, are still prototypes of the first class. The second is represented by *cyanogen* (Döbereiner) ; *prussic acid* (Pelouze) ; *benzonitryle* (Fehling) ; *valeronitryle* (Schlieper) ; *cumonitryle* (Field) ; and several compounds discovered lately by Dumas, Malaguti, and Leblanc. The first instance of the third group was *oxamic acid*, discovered by Balard, to which were soon added numerous members ; by Piria (*melamic acid*), and by Laurent (*tartaramic acid*, *camphoramic acid*) ; and it is to the latter chemist that we are chiefly indebted for a lucid developement of the theory of these acids. The imidogen compounds are as yet the least known : the first, *benzimide*, was discovered many years ago by Laurent, who afterwards found another instance in camphorimide ; cyanic acid (derived from bicarbonate of oxide of ammonium) may also be considered as belonging to this class. With no one acid have all the four classes of compounds as yet been obtained ; with oxalic acid and benzoic acid, we find them best represented : with the former, only *oximide* is wanting, whilst the latter still requires benzamic acid\* for its completion.

Now it appears that these compounds, into which ammoniacal salts are converted by the loss of water, may likewise be obtained with organic bases, or, in other words, (adopting the theory of Berzelius), ammonia, by conjugation, has not lost its original properties, its hydrogen being still capable of elimination by the oxygen of acids.

By distilling oxalate of aniline, M. Gerhardt obtained a compound which he called *oxanilide*, and which, in every respect, represents the *oxamide* of the ammonia series.



With chloride of benzoyl, aniline is converted into an analogue of benzamide.



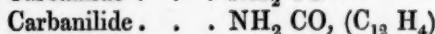
I have performed the same experiment at various periods in the

\* Under this name M. Zinin has described an acid obtained by acting with sulphuretted hydrogen on nitrobenzoic acid ; but, as Berzelius justly observes, this acid should receive another name.

course of these investigations, and can most fully confirm the above statements.

This class of compounds is rapidly increasing, and the anilides seem to be formed even with more facility, and to be more stable, than the corresponding amides.

It is well known that carbamide, produced by the action of ammonia on phosgene gas, cannot be easily separated from the accompanying chloride of ammonium, and that it is very easily decomposed; I found, on the contrary, no difficulty in preparing, by the same process, the corresponding carbanilide, which is moreover a very stable compound.



By acting with bisulphide of carbon on aniline, I obtained sulpho-carbanilide; the corresponding member in the ammonia series is as yet unknown. The same holds good with several other similar compounds.

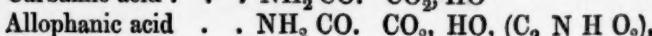
All the bases analogous to aniline will, most likely, show the same comportment. Even now, several naphthalides have been studied by Mr. Delbos, and Mr. Nicholson has pointed out the existence of various cumidides.

The compounds corresponding to cyanogen are as yet scarcely known, probably, because a sufficient number of experiments have not been made with a view to their production.

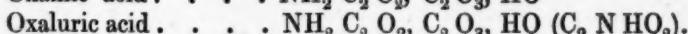
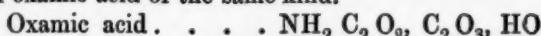
If oxalate of aniline is rapidly distilled, the peculiar odour, which I have repeatedly mentioned, is developed in a most powerful manner.

A mixture of oxanilide and anhydrous phosphoric acid yields, on distillation, a small quantity of this exceedingly pungent compound in the form of oily drops, which, after some time, solidify to a crystalline mass. Unfortunately the largest quantity of oxanilide is charred in this experiment, and the small quantity of the product has, as yet, prevented a close examination of this body. Experiments with chloride of zinc have not given more satisfactory results. This body appears, however, in large quantity among the products of decomposition of dicyanomelaniline, so that I hope soon to be able to give a detailed account of it to the Society.

We know already several conjugated amidogen acids. Allophanic acid, lately studied by Liebeg and Wöhler, is, in the sense of Berzelius' theory, carbamic acid with urea as a conjunct; *i. e.*, it is derived from carbamic acid by the entrance of the same conjunct which converts ammonia into urea, *viz.*, cyanic acid:



In the same manner, oxaluric acid may be considered as a copulated oxamic acid of the same kind.



It deserves to be investigated, whether this acid, which as yet has emerged only from the products of decomposition of uric acid, may not be obtained likewise, either by the dry distillation of an acid oxalate of urea, or by acting with cyanic acid on oxamic acid. Some experiments, which are just now in progress in my laboratory, will, I hope, decide this question.

Conjugated imidogen compounds have not as yet been described; but I may mention, even now, that various substances belonging to this group appear among the products of the decomposition of dicyanomelaniline.

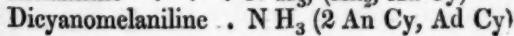
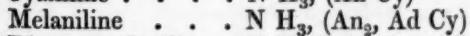
All these considerations render it exceedingly probable that the organic bases are indeed conjugated ammonia-compounds. It is true we are not able, at present, to isolate the ammonia without entirely destroying the compounds; and it is a question whether we shall ever find a method of separating and re-uniting the proximate constituents which the theory of Berzelius supposes in these alkaloids, in the same manner as we effect the separation and re-union of acid and base in a salt. Vainly have I hoped, in the course of my investigations on this subject, to see aniline split up into ammonia and the conjunct



Possibly this separation may succeed in the hands of a more happy experimenter; possibly it may ever remain unaccomplished: nevertheless, the adoption of Berzelius' theory will prove a great benefit, even if it were only to aid the memory and to facilitate the study.

All our formulæ, our whole nomenclature, would be simplified by such an adoption. No longer should we have anilides, naphthalidides and cumidides; these substances becoming anilo-amides, naphthalido-amides, and cumido-amides; and by introducing conventional symbols for the conjuncts, every compound might be expressed rapidly and concisely.

By considering the alkaloids as conjugated compounds of ammonia, cyaniline and melaniline become conjugated ammonia-compounds of the second order, or, in other words, the original ammonia-atom has became associated with the conjunct  $\text{C}_{12} \text{H}_4 = \text{An}$  and with other substances, and the rational formulæ of these compounds now assume the following shape:



XXV. *Ultimate Analysis of some varieties of Coal.* By FRED. VAUX,  
Esq.

The following analyses of several important species of coal were undertaken in the laboratory of King's College, for the purpose of ascertaining their ultimate composition, as well as the nature of the ashes obtained from each.

The varieties of coal subjected to examination, with the respective localities from whence they were obtained, are as follows:

1. Newcastle caking coal, as ordinarily used in the laboratory.
2. Wigan cannel coal, specimen obtained from Professor Miller.
3. Coal from St. Helen's, Lancashire (Rushey Park seam), specimen also from Professor Miller.
4. Staffordshire coal, sample taken last Christmas from the ten-yard seam of a mine near Wolverhampton.
5. Sample from the bottom of the above-named seam in the same mine.
6. Coal from the top of a bed in the Oregon territory.
7. Anthracite (Welsh).
8. Bovey coal, or lignite, from Bovey Heathfield, Chudleigh, near Exeter, Devon.
9. Peat, cut for fuel in 1847, from the neighbourhood of the Military Prison, Princetown, near Tavistock, on the Forest of Dartmoor, Devon.

The respective amounts of the several ingredients were estimated by the following processes.

Moisture—by exposing a known quantity of coarsely pounded coal in a water-bath, kept at  $212^{\circ}$  until it ceased to lose weight.

Coke—by exposing to a bright red heat for about an hour, specimens contained in covered Berlin crucibles, protected from the fire by Cornish crucibles, also covered.

Ash—by exposing the pulverized coke thus obtained in a crucible over the flame of an Argand gas lamp, until all black colour disappeared. This was found to answer very well with all but the Newcastle, which was found to burn with such difficulty, that the following expedient was employed. The coke was heated in an open Cornish crucible, but as a part of the ash acted on the crucible, and adhered to it, the precaution was taken of burning a quantity in the crucible previously, thus forming an interior lining, whereby the weighed quantities were protected from loss.

Sulphur—by the usual process of deflagration with a mixture of 8 parts of nitrate and 1 of carbonate of potash.

Carbon and hydrogen—by burning the dry coal in fine powder

with oxide of copper in German glass tubes, closed at one end, about 60 grains of chlorate of potash being mixed with the oxide nearest the closed end, so as to afford a supply of free oxygen at the end of the process; Liebig's potash bulbs and a chloride of calcium tube being employed to collect the products.

Nitrogen—by the process of Varrentrapp and Will, with soda-lime. The equivalent of the ammonio-chloride of platinum employed in the calculations is 225, and of the sulphate of barytes 117.

#### NEWCASTLE COAL.

The specimen examined was of a blue-black, colour with resinous lustre and cubic fracture, breaking easily on the application of a smart blow, soiling the fingers but slightly, and containing here and there, narrow seams of iron pyrites. On exposure to heat, it lost about one third of its weight, the evolved gas burning with a clear white flame; the coke caked together, swelling considerably, taking the form of the crucible, and a semi-metallic lustre; the fracture was coarse grained. The ash was of a dirty brown colour, very heavy, and fusible without difficulty before the blow-pipe into a black clinker.

The specific gravity of two samples of coal was 1.288 and 1.264, mean 1.276.

*The undried coal gave as follows :*

Experiment.	I.	II.	III.	IV.	
Coal employed.	200	500	500	1000	
Moisture . . . .	2.71	—	—	—	
Coke . . . . :	—	334.5	332.5	—	
Ash . . . . :	—	—	—	20.4	

*By calculation on 100 parts (undried).*

					Mean.
Moisture . . . .	1.355	—	—	—	1.355
Coke . . . . :	—	66.9	66.5	—	66.7
Ash . . . . :	—	—	—	2.04	2.04

*DRY COAL yielded the following.*

Experiment.	I.	II.	III.	IV.	V.	VI.	
Coal employed.	10	10	4.63	8.17	12.6	12.6	
Sulphate of barytes .	0.575	0.518	—	—	—	—	
Carbopic acid . .	—	—	13.82	24.39	—	—	
Water . .	—	—	2.46	4.23	—	—	
Ammonio-chloride of platinum . .	—	—	—	—	4.1	4.2	

*By calculation on 100 parts (dry).*

	I.	II.	III.	IV.	V.	VI.	Mean.
Sulphur . . . .	0.786	0.708	—	—	—	—	0.747
Carbon . . . .	—	—	81.405	81.417	—	—	81.411
Hydrogen . . . .	—	—	5.903	5.752	—	—	5.8275
Nitrogen . . . .	—	—	—	—	2.024	2.074	2.049

WIGAN CANNEL COAL.

The colour of the coal is dark greyish-black, with a resinous lustre and conchoidal fracture; it is less brittle than any other of the specimens. The coal crackles a good deal in the fire, flames much, and burns quickly. When coked, it swells up, and takes the form of the crucible; is hard, and has a semi-metallic lustre. The ash is of a brown colour, not very bulky, fusing (but less easily than the Newcastle) before the blow-pipe into a black clinker.

Specific gravity of the coal 1.276.

*The UNDRIED COAL gave as follows :*

Experiment.	I.	II.	III.	IV.	
Coal employed.	150	300	300	500	
Moisture . . . .	1.36	—	—	—	
Coke . . . .	—	184	182	295.5	
Ash . . . .	—	8	8	13.5	

*By calculation on 100 parts (undried).*

	I.	II.	III.	IV.	V.	Mean.
Moisture . . . .	0.906	—	—	—	—	0.906
Coke . . . .	—	61.33	60.66	59.1	—	60.363
Ash . . . .	—	2.66	2.66	2.7	—	2.673

DRY COAL yielded the following.

Experiment.	I.	II.	III.	IV.	V.	VI.	VII.	
Coal employed.	10	10	10	5.82	7.3	10.15	12.05	
Sulphate of barytes . .	1.0	1.1	1.19	—	—	—	—	
Carbonic acid . .	—	—	—	17.2	21.29	—	—	
Water . . . .	—	—	—	2.92	3.6	—	—	
Ammonio-chloride of platinum . . .	—	—	—	—	—	3.6	3.95	

*By calculation on 100 parts (dry).*

	I.	II.	III.	IV.	V.	VI.	VII.	Mean.
Sulphur . . . .	1.367	1.503	1.626	—	—	—	—	1.498
Carbon . . . .	—	—	—	80.599	79.538	—	—	80.0685
Hydrogen . . . .	—	—	—	5.574	5.479	—	—	5.5265
Nitrogen . . . .	—	—	—	—	—	2.207	2.039	2.123

## ST. HELEN'S COAL.

This specimen was of a black colour, slaty texture, with cubic fracture, resinous lustre, and no pyrites visible.

The coke is infusible, not retaining the form of the crucible, and caking but slightly; it is hard, porous, with a semi-metallic lustre, like plumbago.

The ash is of a reddish-brown colour, sometimes slaty, but the pulverulent part easily fusible before the blow-pipe into a black clinker.

Specific gravity of coal 1.279.

## UNDRIED COAL gave.

Experiment.	I.	II.	III.	IV.	V.	
Coal employed.	100	200	200	300	150	
Moisture . . . .	3.34	6.25	—	—	—	
Coke . . . .	—	—	130	198	—	
Ash . . . .	—	—	—	—	7.5	

## By calculation on 100 parts.

						Mean.
Moisture . . . .	3.34	3.125	—	—	—	3.2325
Coke . . . .	—	—	65	66	—	65.5
Ash . . . .	—	—	—	—	5.0	5.0

## DRY COAL afforded.

Experiment.	I.	II.	III.	IV.	V.	VI.	VII.	
Coal employed.	10	10	7.26	8.56	7.42	13.7	11.34	
Sulphate of barytes . .	0.63	0.69	—	—	—	—	—	
Carbonic acid . .	—	—	20.18	23.82	20.6	—	—	
Water . .	—	—	3.31	4.12	3.5	—	—	
Ammonio-chloride of platinum . .	—	—	—	—	—	4.1	3.63	

## By calculation on 100 parts (dry).

								Mean.
Sulphur . . . .	0.861	0.943	—	—	—	—	—	0.902
Carbon . . . .	—	—	75.807	75.892	75.716	—	—	75.805
Hydrogen . . . .	—	—	5.065	5.347	5.241	—	—	5.217
Nitrogen . . . .	—	—	—	—	—	1.862	1.991	1.9265

## STAFFORDSHIRE COAL.

The specimen was of a brownish-black colour, with a highly resinous lustre, fracture laminated, with a tendency to conchoidal in

the cross grain; the coal does not soil the fingers, has no seams of pyrites, and breaks easily.

The coke swells very much, and cakes into radiating cauliflower-shaped masses; does not take the form of the vessel, is very lustrous, the grain on fracture is small.

The ash is of a yellowish-grey colour, very light, and bulky, but infusible before the blow-pipe.

Specific gravity of two samples of coal 1.28 and 1.277, mean 1.2785.

*The UNDRIED COAL yielded as follows:*

Experiment.	I.	II.	III.	IV.	V.	VI.	VII.
Coal employed.	300	300	500	500	1500	200	200
Moisture . . . .	34.75	33.0	—	—	—	—	—
Coke . . . .	—	—	289	280.5	866.0	—	—
Ash . . . .	—	—	—	—	—	1.75	1.9

*By calculation on 100 parts (undried).*

							Mean.
Moisture . . . .	11.583	11.0	—	—	—	—	11.291
Coke . . . .	—	—	57.8	56.1	57.73	—	57.21
Ash . . . .	—	—	—	—	—	0.875	0.95

*DRY COAL yielded the following.*

Experiment.	I.	II.	III.	IV.	V.	VI.	
Coal employed.	10	10	6.8	7.47	11.88	8.8	
Sulphate of barytes . .	0.29	0.28	—	—	—	—	
Carbonic acid . .	—	—	19.58	21.53	—	—	
Water . . . .	—	—	3.28	3.52	—	—	
Ammonio-chloride of platinum . . .	—	—	—	—	3.41	2.68	

*By calculation on 100 parts (dry).*

							Mean.
Sulphur . . . .	0.396	0.382	—	—	—	—	0.389
Carbon . . . .	—	—	78.529	78.605	—	—	78.567
Hydrogen . . . .	—	—	5.35	5.232	—	—	5.291
Nitrogen . . . .	—	—	—	—	1.786	1.895	1.8405

**STAFFORDSHIRE COAL.**

*Bottom of the seam.*

This coal is of a slaty texture, breaking into laminæ under a smart blow, having a tendency to conchoidal in the cross fracture, considerable quantities of pyrites are visible; in many parts the coal shows very little lustre, but in the conchoidal fractures it is resinous; it does not soil the fingers.

The coke cakes together and swells, but not so much as the last described; it does not take the form of the crucible, while its lustre is more brilliant than the last, and the grain, on fracture, is coarse.

The ash closely resembles that of the last mentioned variety.

Specific gravity of two specimens of the coal 1.278 and 1.274, mean 1.276.

*The undried coal yielded.*

Experiment.	I.	II.	III.	
Coal employed.	300	500	500	
Moisture . . . .	28.0	37.25	—	
Coke . . . .	—	—	291.0	
Ash . . . .	—	—	13.8	

*By calculation on 100 parts (undried).*

				Mean.
Moisture . . . .	9.33	7.45	—	8.391
Coke . . . .	—	—	58.2	58.2
Ash . . . .	—	—	2.76	2.76

*DRIED COAL afforded.*

Experiment.	I.	II.	
Coal employed.	10	10	
Sulphate of barytes .	1.86	1.9	

*By calculation on 100 parts (dry).*

				Mean.
Sulphur . . . .	2.542	2.597	—	2.569

It was considered unnecessary to make any analyses for carbon, hydrogen and nitrogen, since it was taken from the bottom of the seam in the same mine as the last. The chief difference being in the amount of sulphur and ash.

**OREGON COAL.**

The colour of this coal is brownish-black, it is hard, and of a slaty texture, not soiling the fingers, but breaking in laminae.

The coke does not cake or swell, or take the form of the crucible, it is very compact, and but little different from the coal employed.

The ash is also very slaty and compact, of a nearly white colour. Owing to the large quantity of earthy matter in this coal, and the

circumstance that it was only the superstratum of a regular coal bed, it was considered unnecessary to examine it for sulphur, carbon, hydrogen, or nitrogen.

Specific gravity of the coal 1.578.

UNDRIED COAL gave.

Experiment.	I.	II.	III.	IV.
Coal employed.	300	300	300	300
Moisture . . . .	17.0	16.75	—	—
Coke . . . .	—	—	201.0	198.0
Ash . . . .	—	—	100.5	100.5

By calculation on 100 parts (undried).

					Mean.
Moisture . . . .	5.666	5.583	—	—	5.6245
Coke . . . .	—	—	67.0	66.0	66.5
Ash . . . .	—	—	33.5	33.5	33.5

ANTHRACITE.

This species is of a dark iron-black colour and bright metallic lustre, not soiling the fingers, requiring the application of a smart blow to break it when in a large lump, but brittle under the pestle; the principal fracture is more or less slaty, the cross fracture small and imperfectly conchoidal. When heated it burns slowly with a light lambent blue flame, but no smoke; it does not cake, nor does the coke lose any of the metallic lustre, but gradually consumes to a dark grey, not bulky ash, which is infusible before the blow-pipe.

Specific gravity of two samples 1.389 and 1.396, mean 1.3925.

UNDRIED COAL gave.

Experiment.	I.	II.	III.	IV.	V.	VI.
Coal employed.	300	300	400	500	900	450
Moisture . . . .	6.0	6.0	—	—	—	—
Coke . . . .	—	—	366.0	463.5	—	—
Ash . . . .	—	—	—	—	15.5	6.5

By calculation on 100 parts.

					Mean.
Moisture . . . .	2.0	2.0	—	—	2.0
Coke . . . .	—	—	91.5	92.7	92.1
Ash . . . .	—	—	—	—	1.583

DRY COAL gave (*dried at 300° F.*)

Experiment.	I.	II.	III.	IV.	V.	VI.	VII.
Coal employed.	10	10	7.72	7.74	6.17	13.95	10.77
Sulphate of barytes . .	0.66	0.68	—	—	—	—	—
Carbonic acid . .	—	—	25.57	25.67	—	—	—
Water . .	—	—	2.42	2.24	1.75	—	—
Ammonio-chloride of platinum . .	—	—	—	—	—	1.64	1.6

*By calculation on 100 parts.*

							Mean.
Sulphur . . .	0.902	0.929	—	—	—	—	0.915
Carbon . . .	—	—	90.331	90.45	—	—	90.3905
Hydrogen . . .	—	—	3.483	3.215	3.151	—	3.282
Nitrogen . . .	—	—	—	—	—	0.7315	0.924
							0.8277

## BOVEY COAL.

The colour of this coal is earth-brown, with a fibrous and lamellar structure, producing a loud crackling noise either when immersed in water or exposed to the direct rays of the sun, and becoming quite rotten after immersion in water; it does not soil the fingers; the gaseous matters produced by distillation from this variety have a peculiar and extremely nauseous bituminous odour. The coke has a semi-metallic lustre, does not swell, cakes together but slightly, and does not take the form of the crucible; it is easily converted into a bulky red ash, interspersed with white filaments; it is partially fusible, but with difficulty, before the blow-pipe into a black clinker.

Specific gravity of two samples 1.127 and 1.131, mean 1.129.

*The UNDRIED COAL gave.*

Experiment.	I.	II.	III.	IV.	V.
Coal employed.	300	300	800	600	450
Moisture . . . .	104	—	—	—	—
Coke . . . .	—	92.1	245.75	—	—
Ash . . . .	—	—	—	8.7	6.79

*By calculation on 100 parts.*

					Mean.
Moisture . . . .	34.66	—	—	—	34.66
Coke . . . .	—	30.7	30.718	—	30.799
Ash . . . .	—	—	—	1.45	1.470

## DRY COAL gave.

Experiment.	I.	II.	III.	IV.	V.	VI.	
Coal employed.	10	10	8.27	7.72	9.44	11.24	
Sulphate of barytes .	1.736	1.724	—	—	—	—	
Carbonic acid .	—	—	20.1	18.78	—	—	
Water .	—	—	4.2	3.9	—	—	
Ammonio-chloride of platinum .	—	—	—	—	0.86	1.02	

## By calculation on 100 parts.

							Mean.
Sulphur . . . .	2.373	2.356	—	—	—	—	2.364
Carbon . . . .	—	—	66.285	66.344	—	—	66.314
Hydrogen . . . .	—	—	5.642	5.613	—	—	5.6275
Nitrogen . . . .	—	—	—	—	0.566	0.564	0.565

## PEAT.

The specimen was of an earth-brown colour, porous, and largely intermingled with vegetable fibres of a light brown colour, hard enough to be cut with a knife; it did not soil the fingers, and was tough when broken from the interspersed fibres. When heated, the gas gives a brilliant flame with much smoke, the residual coke is much shrunk in bulk, but retains the shape of the pieces employed; it is without lustre and pulverulent, and is readily converted into a light bulky ash of a pure white colour, quite infusible before the blow-pipe.

Specific gravity of two samples of peat .838 and .861, mean .8495.

## The UNDRIED PEAT yielded.

Experiment.	I.	II.	III.	IV.	V.	VI.	
Peat employed.	2625	200	300	300	300	300	
Moisture . . . .	686.0	50.0	—	—	—	—	
Coke . . . .	—	—	86.5	89.34	—	—	
Ash . . . .	—	—	—	—	23.0	20.49	

## By calculation on 100 parts (undried).

							Mean.
Moisture . . . .	26.13	25.0	—	—	—	—	25.565
Coke . . . .	—	—	28.83	29.78	—	—	29.305
Ash . . . .	—	—	—	—	7.66	6.83	7.245

## DRY PEAT yielded.

Experiment.	I.	II.	III.	IV.	V.	VI.
Coal employed.	10	10	9.0	9.66	10.76	13.16
Sulphate of barytes .	0.41	0.41	—	—	—	—
Carbonic acid .	—	—	17.9	19.06	—	—
Water .	—	—	4.02	4.74	—	—
Ammonio-chloride of platinum .	—	—	—	—	4.09	4.73

## By calculation on 100 parts (dry).

							Mean.
Sulphur . . . .	0.56	0.56	—	—	—	—	0.56
Carbon . . . .	—	—	54.242	53.811	—	—	54.026
Hydrogen . . . .	—	—	4.962	5.452	—	—	5.212
Nitrogen . . . .	—	—	—	—	2.365	2.236	2.3005

## ASHES.

	Newcastle.	Wigan cannel.	St. Helen's.	Stafford.	Oregon.	Anthracite.	Bovey.	Peat.
Ash employed.	50	40	50	50	100	35	30	50
Sol. in water . . .	3.5	2.0	5.5	7.0	2.0	2.0	3.23	1.0
Sol. in hydrochloric acid . . .	18.25	12.5	12.5	20.5	10.5	9.0	21.27	36.5
Insoluble . . . .	28.25	25.5	32.0	22.5	87.5	24.0	5.5	12.5

## Calculated on 100 parts.

Sol. in water . . .	7.0	3.0	11.0	14.0	2.0	5.7	10.76	2.0
Sol. in hydrochloric acid . . .	36.5	31.25	25.0	41.0	10.5	25.7	70.9	73.0
Insoluble in acids . . .	56.5	63.75	64.0	45.0	87.5	68.6	18.34	25.0

On passing sulphuretted hydrogen through the hydrochloric solution of the ash, a precipitate was obtained from all the samples, except the Newcastle coal. This precipitate, on further examination, proved to consist of sulphuret of copper or lead; sometimes of both. The following are the indications afforded on dissolving the precipitate in nitric acid, and treating with excess of ammonia.

Cannel, strong blue colour, but no lead.

Oregon, copper and lead slight.

St. Helen's, copper considerable, lead slight.

Anthracite, trace of copper, no lead.

Staffordshire, copper, lead only slight.

Bovey, copper and lead.

Peat, copper and lead, both slight.

The experiments were repeated several times on different samples with the utmost precaution, and ashes of Stafford coal were examined from open fire-places, but all with similar results.

The quantity was ascertained only on peat ash, 200 grains of which afforded 0.048 grains of sulphate of lead = 0.0164 per cent of lead, and 0.04 of oxide of copper = 0.016 per cent of copper in the ash.

TABLE I.  
RELATIVE PROPORTIONS IN 100 PARTS OF UNDRIED COAL.

	New-castle.	Wigan Cannel.	St. Helen's.	Stafford.	Staf. Bottom of Seam.	Oregon.	Anthra-cite.	Bovey.	Peat.
Sp. gravity . . . .	1.276	1.276	1.279	1.2785	1.276	1.278	1.3925	1.129	0.8495
Water . . . . .	1.355	0.906	3.2325	11.291	8.391	5.6245	2.00	34.66	25.565
Gaseous matter . . .	31.945	38.731	31.2675	31.499	33.409	27.875	5.9	34.631	45.13
Coke . . . . .	66.7	60.363	65.5	57.21	58.2	66.5	92.1	30.709	29.305
Ash . . . . .	2.04	2.673	5.00	0.9125	2.76	33.5	1.583	1.479	7.245
Sulphur . . . . .	0.7368	1.4844	0.6728	0.345	2.3534	—	0.8967	1.5446	0.4168
Nitrogen . . . . .	2.0212	2.1037	1.8642	1.6326	—	—	0.8111	0.3691	1.7123

TABLE II.  
RELATIVE PROPORTIONS IN A TON OF UNDRIED COAL.

	New-castle.	Wigan Cannel.	St. Helen's.	Stafford.	Staf. Bottom of Seam.	Oregon.	Anthra-cite.	Bovey.	Peat.
Water . . . . .	c. q. lb. 0.1.23	c. q. lb. 0.2.04	c. q. lb. 0.2.16	c. q. lb. 2.1.1	c. q. lb. 1.2.20	c. q. lb. 1.0.14	c. q. lb. 0.1.16	c. q. lb. 6.3.204	c. q. lb. 5.0.124
Coke . . . . .	13.1.10	12.0.83	13.0.113	11.2.121	11.2.154	13.1.54	18.1.19	6.0.154	5.3.124
Gaseous matters . . .	6.1.152	7.2.278	6.1.04	6.1.502	6.2.204	5.2.82	1.0.204	6.3.20	9.0.3
Sulphate of ammonia* . . .	2.0.182	2.1.02	1.3.27	1.3.0	—	—	0.3.134	0.1.164	1.3.94
Ash . . . . .	0.1.171	0.2.32	1.0.0	0.0.204	0.2.52	6.2.224	0.1.74	0.1.52	1.1.224
Sulphur . . . . .	0.0.162	0.1.54	0.0.194	0.0.72	0.1.243	—	0.0.20	0.1.63	0.0.94

TABLE III.  
RELATIVE PROPORTIONS IN 100 PARTS OF DRIED COAL.

	New-castle.	Wigan Cannel.	St. Helen's.	Stafford.	Staf. Bottom of Seam.	Oregon.	Anthra-cite.	Bovey.	Peat.
Carbon . . . . .	81.411	80.0685	75.805	78.567	—	—	90.3905	66.314	54.0235
Hydrogen . . . . .	5.8275	5.5265	5.217	5.291	—	—	3.283	5.627	5.212
Oxygen . . . . .	7.8975	8.087	11.9825	12.8845	—	—	2.9688	22.861	28.171
Nitrogen . . . . .	2.049	2.123	1.9265	1.8405	—	—	0.8277	0.565	2.3005
Ash . . . . .	2.068	2.697	5.167	1.028	3.011	35.496	1.615	2.269	9.733
Sulphur . . . . .	0.747	1.498	0.902	0.289	2.569	—	0.915	2.364	0.56

TABLE IV.  
RELATIVE PROPORTIONS IN 100 PARTS OF COAL, FREE FROM WATER AND ASH.

	New-castle.	Wigan Cannel.	St. Helen's.	Stafford.	Staf. Bottom of Seam.	Oregon.	Anthra-cite.	Bovey.	Peat.
Carbon . . . . .	83.1301	82.2878	79.9352	79.388	—	—	91.8742	67.8535	59.7377
Hydrogen . . . . .	5.9505	5.6796	5.5012	5.3459	—	—	3.3368	5.7576	5.7739
Oxygen . . . . .	8.0647	8.3113	11.5811	13.0185	—	—	3.0178	23.392	31.3196
Nitrogen . . . . .	2.092	2.1818	2.0314	1.8596	—	—	0.8412	0.5781	2.5486
Sulphur . . . . .	0.7627	1.5395	0.9511	0.393	2.6487	—	0.93	2.4188	0.6208

\* \* Calculated on the supposition that the whole of the nitrogen is converted into ammonia, which in practice, is not the case.

The following Table gives the calculated results on the annexed approximative empirical formulae for each of the preceding varieties of coal, at the same time exhibiting their agreement with the quantities of carbon, hydrogen and oxygen found by analysis in Table IV.

Formula.	Newcastle.		Wigan Cannel.		St. Helen's.		Stafford.		Anthracite.		Bovay.		$C_{30}H_{11}O_8$	
	$C_{27}H_{11}O_2$		$C_{28}H_{10}O_2$		$C_{29}H_{11}O_3$		$C_{30}H_{10}O_3$		$C_{40}H_8O$		$C_{27}H_{14}O_7$		$C_{29}H_{11}O_8$	
	Calc. <sup>a</sup> .	Found.	Calc. <sup>a</sup> .	Found.	Calc. <sup>a</sup> .	Found.	Calc. <sup>a</sup> .	Found.	Calc. <sup>a</sup> .	Found.	Calc. <sup>a</sup> .	Found.	Calc. <sup>a</sup> .	Found.
Carbon . .	83.26	83.1301	82.52	82.2878	80.28	79.935	80.25	79.383	92.08	91.874	67.73	67.8535	59.58	59.7377
Hydrogen . .	5.654	5.9505	5.289	5.6796	5.256	5.5012	5.144	5.3459	3.069	3.3368	5.853	5.7576	5.462	5.7739
Oxygen . .	8.223	8.0647	8.463	8.3113	11.47	11.5811	12.348	13.018	3.069	3.0178	23.412	23.392	31.78	31.3196

*On the analyses of some specimens of hot and cold blast iron, by F. C. Wrightson, Esq.*—THE specimens of iron, of which the following are analyses, were kindly furnished by Richard Smith, Esq., agent to Lord Ward, from the Coneygre iron furnaces, near Dudley. The object of the analyses was to show how far the quality agrees with what might be predicated from the composition, and also the difference produced in the composition of the iron by the cold, warm, and hot blasts respectively, when smelted from the same, or nearly the same, materials. The materials manufactured by the hot blast only differed in having a small proportion of an ore richer in iron added to the others; and it is probable that the essential difference in the per centage of silica contained in two, and of the phosphorus in all, is due to the effect of the hot blast. The phosphoric acid, for example, requiring a very high temperature for its reduction. Of Nos. 2 and 4, (see table below) the *hot blast* iron is considered much inferior, being more brittle than the others, and requiring much longer working in the puddling furnace. No. 8 (*hot blast*) is also considered a very inferior iron, for, although it contains but little silica, a larger proportion of phosphorus enters into its composition. This, however, as well as the warm and cold blast of the same number, is liked by the workmen (*puddlers*), on account of the yield, they being paid by the quantity produced; and this, as will readily be seen, must be greater than from the lower numbers.

*Method of analysis.*—For the determination of the first five constituents, silica, &c., the iron was broken up in a steel mortar until sufficiently small to be readily acted upon by hydrochloric acid, and by nitric acid. One portion was weighed for the estimation of the silica, iron, and manganese, and a second portion for sulphur and phosphorus.

*Silica, &c.*—The first portion of the iron was treated with hydrochloric acid in a sand-bath, until nothing but silica and carbon remained undissolved; it was then evaporated to dryness, strongly heated, and again treated with hydrochloric acid. The silica thus separated, generally contained a little iron, and was also *intimately* mechanically combined with carbon. It was, therefore, removed from the filter, and fused with carbonate and nitrate of potash; the silica, again separated in the usual way, was dried, ignited, and weighed. The iron was added to the main quantity in solution, which was then boiled with nitric acid. Ammonia was added to the solution until a faint acid reaction alone remained, when a little succinate of ammonia sufficed to precipitate the iron which remained in solution. The succinate of iron thus separated, was filtered off, well washed with cold water and ammonia, dried, ignited, and weighed. It was then moistened again with nitric acid, dried and ignited, until the weight became constant. The solution was then evaporated, sulphuret of ammonium added to it, and the whole allowed to stand for twelve hours; the sulphuret of manganese was then filtered off, and washed with water containing sulphuret of ammonium. The sulphuret was

converted into sulphate, dried, ignited, and weighed. The solution from which the sulphuret of manganese had been separated still contained a little more sulphuret of manganese, which was proved by evaporating it to dryness, igniting, and driving off the ammoniacal salts, when the manganese was left in the form of sesquioxide ( $Mn_2 O_3$ ). This was converted first into protochloride of manganese, and then into sulphate of the protoxide, and added to the first quantity.

*Sulphur and phosphorus.*—The second portion of iron being treated with fuming nitric acid, and warmed, quickly dissolved, the silica was separated in the usual manner. Chloride of barium was then added to the mass re-dissolved in hydrochloric acid, and after standing for twenty-four hours, the sulphate of barytes was separated. The excess of barytes was then removed by sulphuric acid, and a sufficient quantity of tartaric acid mixed with the solution to prevent the precipitation of iron, when ammonia was added in *excess*. Sulphuretted hydrogen was then passed through the solution, until all the iron was precipitated as sulphuret of iron, and being allowed to stand warm for twelve hours, until it became of a bright yellow colour, (sulphuret of ammonium being present in excess), the sulphuret of iron was separated, and well washed with hot water containing sulphuret of ammonium. The filtered solution was evaporated to dryness, carefully ignited, so as to expel the ammoniacal salts, and then burn away the tartaric acid. The residue which remained in the platinum dish consisted of phosphate of ammonia, (with generally a little impurity). It was fused with an excess of carbonate of potash and soda. The fused mass was treated with boiling water, which dissolved nearly the whole of it. Hydrochloric acid was added in excess to the filtered solution, which was then boiled. The phosphoric acid was precipitated by sulphate of magnesia and an excess of ammonia, with the usual precautions. From the quantity of ammonia-phosphate produced, the phosphorus was calculated.

It was attempted, in the first analysis, to separate the iron without the use of tartaric acid, by passing sulphuretted hydrogen for a long time through the precipitated peroxide of iron (ammonia being in excess) at a high temperature, but more phosphoric acid was several times separated from the same portions of iron by the process described.

*Nitrogen* being detected in minute quantity in several of the specimens by Varrentrapp and Will's process, it was at first thought necessary to determine it in all; but the extremely small quantity found in others, as well as the great tediousness of reducing the iron to powder, induced me to relinquish its estimation.

*Carbon* was determined by grinding in an agate mortar about 30 grains of filings of the iron (obtained by using one of the *hardest* Sheffield files, which itself loses but a very minute quantity in the process), with a portion of *pure white* sand (previously treated with nitric acid, &c., to destroy any traces of vegetable matter) until the whole was reduced to a perfectly impalpable powder. *Chromate of lead*, and *oxide of copper*,

with chlorate of potash, were both used in the process of analysis, the preference however was given to the former, as affording, in several trials, a greater per centage of carbon.

*Analysis of 12 specimens of "Cast Iron from the Furnace;" three kinds, "Cold," "Warm," and "Hot Blast," 4 qualities of each, 2, 4, 6, 8.*

COLD BLAST.

2.	4.	6.	8.
Silica . . . 3·51	Silica . . . 3·45	Silica . . . 1·79	Silica . . . 1·37
Iron . . . 92·98	Iron . . . 90·61	Iron . . . 93·53	Iron . . . 95·67
Manganese . . . 0·49	Manganese . . . 0·91	Manganese . . . 0·95	Manganese . . . 0·35
Sulphur . . . 0·99	Sulphur . . . 0·30	Sulphur . . . 0·39	Sulphur . . . 0·36
Phosphorus . . . 0·47	Phosphorus . . . 0·41	Phosphorus . . . 0·31	Phosphorus . . . 0·20
Nitrogen . . . —	Nitrogen . . . —	Nitrogen . . . 0·25	Nitrogen . . . —
Carbon . . . 2·31	Carbon . . . 2·19	Carbon . . . 2·04	Carbon . . . 1·79
100·75	97·87	99·26	99·74

WARM BLAST.

Silica . . . 3·09	Silica . . . 2·89	Silica . . . 1·33	Silica . . . 1·57
Iron . . . 92·45	Iron . . . 91·82	Iron . . . 94·20	Iron . . . 95·08
Manganese . . . 0·54	Manganese . . . 0·91	Manganese . . . 0·50	Manganese . . . 0·79
Sulphur . . . 0·57	Sulphur . . . 0·26	Sulphur . . . 0·20	Sulphur . . . 0·45
Phosphorus . . . 0·40	Phosphorus . . . lost.	Phosphorus . . . 0·54	Phosphorus . . . 0·38
Nitrogen . . . —	Nitrogen . . . —	Nitrogen . . . —	Nitrogen . . . —
Carbon . . . 1·96	Carbon . . . 2·76	Carbon . . . 2·11	Carbon . . . 2·28
99·01	98·64	98·88	100·55

HOT BLAST.

Silica . . . 5·14	Silica . . . 5·06	Silica . . . 1·57	Silica . . . 1·34
Iron . . . 90·76	Iron . . . 91·30	Iron . . . 94·31	Iron . . . 95·64
Manganese . . . 0·79	Manganese . . . 0·69	Manganese . . . 0·79	Manganese . . . 0·39
Sulphur . . . 1·07	Sulphur . . . 0·28	Sulphur . . . 0·20	Sulphur . . . 0·33
Phosphorus . . . 0·51	Phosphorus . . . 0·55	Phosphorus . . . 0·50	Phosphorus . . . 0·71
Nitrogen . . . trace.	Nitrogen . . . —	Nitrogen . . . —	Nitrogen . . . 0·10
Carbon . . . 2·87	Carbon . . . 2·09	Carbon . . . 1·82	Carbon . . . 1·59
101·14	99·97	99·19	100·10

XXVI. *On the argument for the Binary Theory of Salts, derived from the Non-action of the Anhydrous Oxygen Acids on Organic Colours.* By GEORGE WILSON, M.D., F.R.S.E., Lecturer on Chemistry, Edinburgh, &c., &c.\*

In a paper recently read to the Royal Society of Edinburgh,† which will be published in the forthcoming number of their transac-

\* This paper was read on the 15th of May, 1848.

† April 17, 1848.

tions,\* I have detailed a series of experiments made with the dry gases on dry colouring matters. The object for which these experiments were undertaken, was to supply a defect in the theory of bleaching; but certain of them having a bearing on the binary theory of salts, which I have not discussed in the paper referred to, I am anxious now to lay them before the Chemical Society.

One of the arguments, though assuredly not the most important employed in the defence of the theory of salts in question, is derived from the fact that the so-called oxygen acids, when anhydrous, do not redden dry litmus. The reddening action which they exhibit when moist, is supposed by those who make use of the argument under notice, to be dependent on their appropriating the elements of water, so as to become hydrogen acids of new radicals. It appears to be implied in this view, that a hydrogen acid, whether solid, liquid, or gaseous, possesses, *per se*, a power of reddening blues, and that the reddening action of the hydrated oxygen acids, is mainly owing to their containing hydrogen.

The defenders of the binary theory of salts do not lay great stress on this argument, or profess to be able to demonstrate that it has a basis in fact, but they nevertheless attach to it a certain value, which has not however been exactly defined. It seems desirable accordingly, to determine, if possible, what that worth is.

There is no doubt of the fact, that certain at least of the oxygen acids lose all action on colouring matter when deprived of water; and if I do not extend this observation to all of them, it is simply because I cannot find records of experiments on this property of acids having been tried with more than a few of them. The point, however, which I wish to bring before the Society, can be illustrated as well by reference to one acid as to many, and I shall select sulphurous acid as the one to be commented on.

Sulphurous acid, which, when moist, reddens litmus with great rapidity, can easily be rendered at ordinary temperatures, (for example, at 60° F.) anhydrous, or at all events, so dry, that it exerts no action on equally dry litmus. In proof of this, if proof be needed, I may mention that I have in my possession a sealed tube, containing dried litmus paper and gaseous sulphurous acid, which have remained in contact since July 1847. After the lapse of nine months, the blue remains unchanged. This is a sufficiently striking example of the indifference of a dry oxygen acid to colours. For comparison with it, I mention an exactly similar experiment made with a hydrogen acid. In July of the same year, I shut up dried

\* Vol. xvi, Part iv.

hydrosulphuric acid (sulphuretted hydrogen) with blue litmus, and brown rhubarb paper. At the present date, (May, 1848) with the exception of a few very small red spots on the blue, the papers are unchanged in tint. More recently I have preserved blue litmus for a month in dry sulphuretted hydrogen, without the slightest alteration in tint occurring. From these observations it appears, that there is, at least, one hydracid whose action on vegetable blues is as effectually arrested, by depriving it of water, as that of sulphurous acid. Hydrosulphuric acid unquestionably is not one of the most powerful reddeners of blues; its action on these, however, is well marked, and is certainly as great as that of hydrated carbonic, or boracic acid. It would seem then, that the presence of hydrogen in an acid, is not sufficient to confer upon it the power of reddening blues, and it becomes equally questionable, whether it is the absence of hydrogen from dry gaseous sulphurous acid which renders it indifferent to colours.

It will not be questioned by any one, that the argument from colours for the binary theory is seriously affected by the fact I have mentioned, and that the inference must be qualified, or adjusted, so as to be reconcilable with the indifference of a dry hydracid to vegetable blues. A little reflection will shew, that the argument under discussion unwarrantably takes for granted, that in depriving an oxygen acid of water, we leave all the conditions of chemical action as they were before, *minus* the presence of water. We plainly, however, do not; for, when we dry sulphurous acid, for example, we do something more than merely make it non-aqueous; we convert it, when the experiment is made at ordinary temperatures, into a gas, and the condition of elastic fluidity is greatly less favourable to chemical action, especially when colouring matters are concerned, than that of mediate liquidity, which water gives to the gases which it dissolves. We must manifestly make allowance for this certain cause of delayed or negative action of gases on colours; and shew further that it is not sufficient to account for the indifference which a dry gaseous oxygen acid exhibits to these, before, in the face of the fact that anhydrous hydrosulphuric acid does not redden blues, we speak of the absence of hydrogen from an oxygen acid as the cause of its not changing colours.

Similar observations, *mutatis mutandis*, apply to those oxygen acids, which, like the sulphuric or iodic, assume the solid form when rendered anhydrous. The conditions of chemical action are much less favourable when the solid acid and solid litmus are brought into physical contact, than when the colour is dissolved in

the hydrated acid; and we are not entitled to attribute the non-action of the crystalline dry acid to the absence of hydrogen, or of the elements of water, considered as changing the body merely chemically, till we are able to shew that the alteration in physical form is not of itself sufficient to prevent chemical action.

I have purposely left for latest consideration, the condition of liquidity, into which it is possible to throw most of the dry oxygen acids, by lowering or increasing their temperature, or by exposing them to the pressure of their own vapours. Anhydrous sulphurous acid for example, is very easily reduced to the liquid state, and in this form, if in any, admits of direct comparison as to its action on colours with the same body dissolved in water. It is from the action of the *liquid* anhydrous acids alone that arguments can be drawn for or against the binary theory of salts, and here I have to lament that I have not been able to find any reference of an unexceptionable kind, to the action of even one of the liquefied gases on dry colours. In the absence of such records, I bring before the Society a result which appears to me very interesting, obtained with liquefied sulphurous acid. That an estimate may be formed by all of the exact value of this experiment, I mention the mode in which it was made, somewhat particularly.

The great point aimed at, was, to render the colouring matter and the acid as dry as possible. For this purpose, a small slip of the thinnest writing paper was stained with a strong infusion of blue litmus, and enclosed in a bulb, blown on a thin tube open at both ends. The paper was then raised to the temperature of  $280^{\circ}$  F., and a current of air, which had been passed through a freezing-mixture, and a long tube filled with fused chloride of calcium, sent over it for three hours. The thin tube containing the paper was ultimately sealed at both ends, before detaching the drying apparatus, so as to enclose the paper within the bulb. The bulb, thus provided, was placed within a wide tube of strong glass, which was afterwards drawn out at both extremities into narrow canals, bent twice at right angles, so as to admit of its being immersed in a freezing-mixture. This tube was connected by caoutchouc collars, with a desiccating arrangement, by means of which air was supplied in a current, so as to dry the inside of the tube, and the outside of the bulb. The greater part of the drying apparatus was then removed, and replaced by a fresh one, through which the sulphurous acid was transmitted. This gas, which was prepared by the action of mercury on oil of vitriol, was passed through a washing-bottle, containing water, then through oil of vitriol, and a long wide

tube, filled with fused chloride of calcium. As soon as a considerable quantity of the gas had become liquid in the tube containing the bulb, which was immersed in a mixture of powdered ice and salt, the ends of the tube were sealed at the blow-pipe, and the former removed from the freezing-mixture. The tube was then shaken, till the bulb within broke, and allowed the paper and acid to come together. The paper was immediately soaked through, and thoroughly wetted, but it remained of the purest blue. The result was witnessed by four persons besides myself. No alteration in tint occurred for five minutes, during which I watched it. The tube was then restored to the freezing-mixture, which was not, however, replenished, and I did not see the paper again for an hour and a quarter. At the end of this period, I found that its tint had changed to a very dark purple. When seen for the third time, some twenty hours later, the paper had become of the brightest red.

Three explanations suggest themselves as to the ultimate reddening of the paper: 1st. The sulphurous acid, or the paper, or both, may not have been absolutely anhydrous. 2ndly. The affinity of sulphurous acid for water, may have determined the generation of that liquid out of its elements contained in the coloured paper. 3rdly. Liquid sulphurous acid may be able to redden blue litmus, although the gaseous acid cannot.

Of these views I prefer the second. It is quite possible that neither the gas nor the paper was quite dry. Till we possess a test of absolute dryness, applicable especially to gases, it is impossible to speak decidedly on this point. I am not prepared, therefore, to affirm, that water was certainly altogether absent; but if a sufficient quantity of ready formed water had been present from the first, there seems no reason why the acid should not have reddened the blue within a few seconds, whereas even in an hour, it had developed only a dark purple. It is true that during that lapse of time, the tube was at a temperature sufficiently low to solidify water, if that body were present, and it is possible that as the freezing-mixture liquefied, and rose to the temperature of the air, it left the water free to act in a way it could not do when congealed. But the acceptance of this view tells all the more in favour of the conclusion, that liquid sulphurous acid, not containing *liquid* water, cannot redden vegetable blues. I am inclined, however, to think, judging from my experiments with *gaseous* sulphurous acid, that in the trial with it liquefied, the acid and the paper made too near an approximation to absolute dryness to warrant the inference that the slow reddening was owing to the presence of ready formed water. It seems more

probable, that the gradual change in colour corresponded to an equally gradual development of water from its elements present in the coloured paper. Such a production of water, where it did not pre-exist ready formed, is familiar to every chemist, as occurring when bodies containing its elements, are brought into contact with acids, alkalis, salts, or other substances which have a great affinity for that liquid.

The third view suggested, seems contradicted by the fact that the reddening of the paper was not instantaneous, or at least not very speedy, although it was completely wetted and saturated by the acid. It appears to me, therefore, that a strong argument may be derived from the primary negative action on colour, of liquid sulphurous acid, in favour of the binary theory of salts, although its force is certainly weakened by the fact that the paper is eventually reddened; and that it is not certain that ready formed water was altogether absent. I do not, however, think it probable, that even if absolute dryness were secured, we should succeed in preserving for any length of time, a vegetable blue unreddened, in contact with a liquid having such a disposing power over the elements of water as sulphurous acid probably possesses. The same remark applies, *mutatis mutandis*, to other bodies, such as hydrochloric acid and ammonia, although it does not appear improbable, that substances having a weaker affinity for water, such as carbonic acid, might be retained in the anhydrous liquid form, over vegetable colours for indefinite periods, without changing their tints. A series of researches into the action of the liquefied anhydrous gases on anhydrous organic colours, would be a very valuable contribution to chemical science.

Till such trials are made, we can, I fear, make little, if any use of the non-action on colours of gaseous or solid acids, as an argument in favour of the binary theory of salts. We are not at liberty, moreover, to infer, that the action of a liquefied gas is identical with that of the same gas, meditately liquefied by water. The properties of liquid and solid carbonic acid, for example, the best known of the condensed gases, so far as they have been examined, appear greatly different from those of the same body when in aqueous solution; and, that relation to colour is one of the characters which will be most affected by the absence of water, may certainly be inferred, alike from a consideration of the properties of that liquid, and from other familiar facts. Water, when it meets a colouring matter, such as litmus, in the first place wets it completely, and rises into its pores, so as to come into a closeness of

physical contact with it, highly favourable to chemical action. 2ndly. Water dissolves litmus; in other words, liquefies it. 3rdly. Water dissolves all the gases which affect organic colours. In the presence of this fluid accordingly, the gas and colour *both* assume the liquid form, a physical condition much more favourable for chemical action than if the one only were liquid and the other solid or gaseous. Unless, therefore, a liquefied gas have as great an adhesive attraction for colouring matter,\* and as great a solvent power over it as an aqueous solution of the gas possesses, the former may not equal the latter in action upon the colour, although it has the advantage over the watery liquid of being more concentrated. It is not, for example, likely that liquid carbonic acid has a wetting and a solvent power over organic bodies equal to those of water, and its probable defect in this respect must be one source of its presumed indifference to colours, although it may not be the only cause of its negative action on them.

I have already mentioned, that liquid sulphurous acid wetted paper readily. It may have wetted it, however, without equally wetting the litmus, and this may have been one cause of its delayed action on the latter. The acid acquired no colour after remaining for a fortnight in contact with the litmus paper. It is possible, however, that it may have dissolved some of the colouring matter, but that at the same time it bleached it, so that no tint was given to the acid. If any colouring matter, however, was dissolved, its quantity must have been exceedingly small, for the paper remained of a full red, and exhibited no traces of bleaching.

In further illustration of the difference between the action of an aqueously dissolved, and a pure liquefied gas, I may mention that I have found that anhydrous liquid bromine bleaches blue litmus much more slowly than it does when hydrated. Each one of the liquefied gases, in like manner, has probably an adhesive attraction and a solvent power for colours different from those of water, and in all likelihood specific. Each, accordingly, will require experiments for itself, and it seems improbable that any of them will prove identical in character with their aqueous solutions.

I urge this on general considerations, but facts in proof of it can, I think, be easily adduced. The non-action, for example, of gaseous sulphuretted hydrogen on vegetable blues, as contrasted with its action on these when dissolved in water along with them,

\* The term adhesive attraction is to be understood here as not merely referring to the wetting of the superficies of a mass, but likewise to the internal wetting of a porous solid, generally spoken of, as occasioned by "capillary attraction."

is, in all probability, a case of chemical affinity inactive, owing to the absence of favourable physical conditions. The gaseous acid comes only into slight contact with the solid ; it cannot wet the paper, and it cannot dissolve the colouring matter. The presence of hydrogen in it, and the fact of its being a perfect hydracid, are not sufficient to overcome obstacles to chemical action so powerful as these. I have, in like manner, found, that even hydrochloric acid, although it cannot be preserved in the gaseous form over vegetable blues without ultimately reddening them, may be sent in a current for five minutes over litmus without sensibly changing its tint, and that it requires the lapse of some hours before it exhibits, what we are accustomed to consider, its characteristic action on vegetable colours. For the particulars of the experiments made on this subject, I refer to the paper mentioned at the beginning of this communication.

The strongest, then, of the hydrogen acids, is at least indebted to the assistance of water for its power to redden blues instantaneously, and perhaps, but for its power to generate water out of its elements, would not, in the gaseous anhydrous form redden them at all. In further illustration of this point, I would refer to the well known negative bleaching action of dry gaseous chlorine, which is so marked, that I have preserved litmus paper for nine months in an atmosphere of this gas without the tint being materially altered.\* I have sought to prove in discussing the theory of bleaching, that the negative action of anhydrous chlorine when gaseous, is entirely attributable to a change in physical condition, such as I have referred to in the preceding remarks on the non-action on colours of dry sulphuretted hydrogen.

The general conclusion seems fairly deducible, from the facts and considerations I have urged, that the removal of water from an oxygen acid, alters most materially its physical as well as its chemical relations ; and that in the present state of our knowledge we are not in a condition to decide, whether it be the physical or chemical change in the acid which most, or altogether, determines the change in its actions on organic colours.

\* In this experiment, the sealed tube containing the paper and chlorine was purposely excluded from direct sun-light. When exposed to the sun-beam, dry chlorine bleaches with considerable rapidity. In illustration of this, see paper in Edinburgh Philosophical Transactions, section "On the influence of sun-light on the bleaching action of dry Chlorine."

## NOTICES

OF

### PAPERS CONTAINED IN THE FOREIGN JOURNALS.

*On aqua-regia.* By M. GAY-LUSSAC.\*—Since the time of Berthollet, most chemists have considered aqua-regia, or the mixture of nitric and hydrochloric acids, in variable proportions, as composed of free chlorine and nitrous gas, held in solution by the two acids, and more particularly by the nitric acid. Berthollet also showed that chlorine and nitrous gas combine at the moment of mixture, and are subject to a considerable condensation of volume. After 50 years of silence upon this point, Edmond Davy discovered that when nitric acid is allowed to act upon common salt, a gaseous mixture is evolved of an orange-yellow colour, which contains chlorine, and another gas easily absorbable by water. He likewise pointed out the similarity of this gaseous mixture to the condensable compound of chlorine and nitrous gas of Berthollet, and was led by his experiments to the conclusion that the gas was composed of equal volumes of chlorine and nitrous gas, united without condensation. Baudrimont here took up the investigation, and condensed into a reddish-brown liquid, by means of a freezing-mixture, the gas evolved from aqua-regia. His analysis of the compound induced him to assign it the formula—



and to substitute the name of chloronitric acid in place of chloronitrous acid, given to it by Davy. This compound was considered by Baudrimont as the active principle of aqua-regia. Notwithstanding these experiments, the majority were still in the habit of viewing aqua-regia, with Berzelius, in the same light as it was viewed by Berthollet. The composition of M. Baudrimont's compound, and the theory of its formation from the elements of aqua-regia, gave no explanation of the simultaneous production of chlorine, which was invariably observed by all who have studied this acid mixture.

M. Gay-Lussac has collected the gases evolved from aqua-regia at the temperature of boiling water; and, passing them through a cooling-mixture, has succeeded in condensing a cloudy lemon-coloured liquid, very different in appearance from a mixture of nitrous vapour and chlorine, while chlorine gas passed off.

This liquid was completely decomposed by water, without the evolution of any gas, and the solution contained hydrochloric acid, but no free chlorine. The amount of chlorine in the original gas was ascertained by

\* Ann. de Chim. et de Phys., xxxiii. 203.

precipitating the aqueous solution with nitrate of silver, and the relation which it bore to the other compound of nitrogen and oxygen was that of 2 equivs. to 1 equiv.

An analysis of the gas by means of mercury, which absorbed the chlorine, led to the same result, and confirmed the identity of the nitrogen compound with nitric oxide. The composition of the liquid is, therefore, expressed by the formula—



and this perfectly explains the simultaneous evolution of chlorine ; 3 equivs. of oxygen, separating from an equivalent of nitric acid, give rise to 3 equivs. of chlorine, 2 of which remain in combination with the nitric oxide, and produce the new liquid acid, or *hypochloronitric acid*, while the other is liberated.

Aqua-regia, however, prepared under different circumstances, affords liquid products, which are by no means of such constant composition. When the muriatic acid of the mixture is replaced by common salt only just covered with the ordinary nitric acid of commerce, 2 equivalents of chlorine to 1.30 equivs., and in another case to 1.53 equivs. of nitric oxide were obtained from the vapour of the liquid. When gold is acted upon by aqua-regia, the nitric oxide in the mixture is reduced to somewhat less than 1 equivalent. These facts, and the different relative proportions of the two gases obtained from successive portions of the liquid, shew that the body is a mixture, and that  $\text{NO}_2 \text{Cl}_2$  is not the only constituent of the chloronitric liquid. There is at least one liquid in the condensed products from aqua-regia possessing the composition shewn by the formula—



which latter may also be obtained directly by allowing nitric oxide and chlorine to condense together in a vessel surrounded by a cooling-mixture : but even then the product is not a definite body, for the proportions of nitric oxide gas in the less volatile portions are very much greater than in the more volatile. The same results were obtained from the vapour of the liquid condensed from a mixture of common salt with nitric acid.

These condensed liquids, prepared in different manners, are, therefore, mixtures in variable proportions of the two compounds,  $\text{NO}_2 \text{Cl}_2$ , and  $\text{NO}_2 \text{Cl}$ .

The products bear a great analogy to the hyponitric and nitrous acids, and it is proposed to call them *hypochloronitric acid* and *chloronitrous acid* respectively. They are both decomposed immediately by water, and give rise to hydrochloric acid and the products of hyponitric acid.

Aqua-regia, therefore, whether concentrated or diluted, without the agency of any other body, and simply under the influence of heat, is decomposed into chloronitric vapour, chlorine and water.

When gold is acted upon by aqua-regia, the author's experiments tend to shew that the products of decomposition are precisely the same, the chlorine only being retained by the gold and the chloronitric vapour, to which the action of aqua-regia upon gold has been erroneously attributed, passing off as if no gold were concerned in the reaction.

*On asparagine and aspartic acid.\**—Piria has established the fact, that asparagine is produced in equal abundance from vetches that are allowed to germinate in the light as from those growing in the dark; that the production of this substance in the plant is confined to the period of germination and growth, the seeds containing no asparagine, while mere traces are obtained from the plant after flowering, and none after fruition.

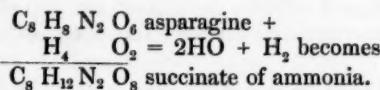
To produce asparagine, the juice of the vetch is expressed and evaporated, the albuminous matter which coagulates is separated by filtration, &c., the filtrate left to itself for six hours, deposits crystals of asparagine, which are purified by re-crystallization. Asparagine, contrary to the experience of other chemists, is an acid capable of reddening litmus, and expelling acetic acid from combination. It forms a difficultly soluble compound with oxide of copper, in which the oxide replaces an equivalent of water; the analysis of this salt led to the formula:



and when decomposed with sulphuretted hydrogen, pure crystallized asparagine was again obtained, the composition of which is expressed by:



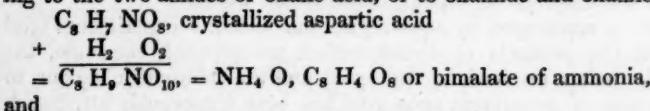
A solution of pure asparagine in water, when left to itself, undergoes no change, but if the substance is still coloured, a fermentative process ensues, which in the course of a short time converts the whole of the asparagine into succinate of ammonia. The asparagine assimilates under the reducing agency of fermentation, two equivs. of water and two equivs. of hydrogen. Thus:



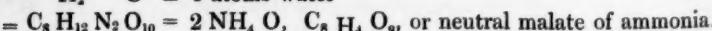
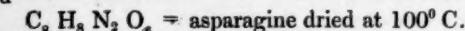
Oxidizing agents, as nitric and chromic acids, are not capable of re-converting the succinate of ammonia into asparagine. The nitrogenous matters to which the fermentation of asparagine is due, are contained in the juice of the vetch.

Asparagine is converted by hydrochloric, sulphuric, and even by nitric acid that is free from peroxide of nitrogen, into ammonia and aspartic acid, and the aspartic acid thus formed is not changed, as has been supposed by Liebig and others, on again being treated with pure acid. The aspartic acid, which is very insoluble in water, dissolves readily in hydrochloric acid, and has given rise to the supposition that it was changed into a more soluble acid. Aspartic acid is represented by the formula  $\text{C}_8\text{H}_7\text{NO}_3$ .

Asparagine and aspartic acid are both decomposed by the action of peroxide of nitrogen into pure nitrogen gas, which is evolved, and water and malic acid, which remain in solution. This result leads to the conclusion that the two bodies may be regarded as amides of malic acid, corresponding to the two amides of oxalic acid, or to oxamide and oxamicacid. For:

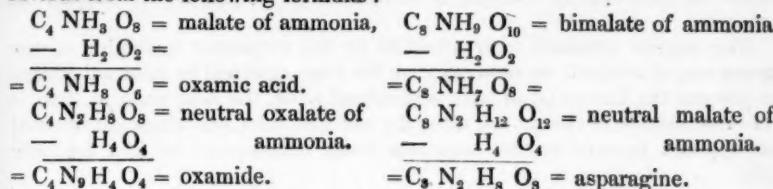


and



\* Ann. de Chim. et de Phys., xxii. 60.

The analogy between the amides of malic and oxalic acids, will be obvious from the following formulæ :



*On the neutral salts of uric acid.\**—Drs. Allan and Bensch have succeeded in replacing the atoms of water in crystallized uric acid, by several other bases besides the alkalies, and thus preparing a series of neutral urates, which are represented in the anhydrous state by the general formula,  $MO, C_6 N_2 HO_2$ . The neutral urates of potash and of soda are prepared by adding uric acid to caustic solutions of these alkalies, as long as the acid is dissolved in the cold, and then boiling the solution thus obtained in a retort until a deposit of fine crystalline needles begins to subside, collecting these, and washing them first with dilute, and subsequently with stronger alcohol.

A neutral salt of ammonia could not be obtained. A gelatinous precipitate, consisting probably of neutral urate of magnesia, was prepared by adding a dilute solution of neutral urate of potash to a boiling solution of a salt of magnesia. On re-boiling this precipitate with water, however, magnesia is separated, and an acid salt remained in solution. Alcohol also precipitated an acid salt from the above mixed solution.

The experiments, instituted with the view of obtaining double salts of magnesia with potash, soda, or ammonia, were unsuccessful.

Urates of lime, barytes and strontian, are obtained in the purest form by boiling solutions of these bases with uric acid, when the neutral salts are deposited in a granular form. Neutral urate of lead is obtained by adding neutral urate of potash to a dilute solution of nitrate of lead, the yellow precipitate, which is formed at first, is separated by filtration, and the white amorphous insoluble powder, which is formed by a further addition of urate of potash, is collected and washed with alcohol or water, in both of which it is perfectly insoluble.

Salts of the other metallic oxides—as protoxide and peroxide of iron, oxide of copper, oxide of nickel, protoxide of manganese—could not be prepared by the processes described above.

The neutral salts of uric acid are easily decomposed by the carbonic acid of the atmosphere; they must consequently be dried for the purpose of analysis in a current of dry hydrogen gas. The relations of solubility were established by filtering the different solutions, either hot or cold, into a bottle of known capacity, evaporating afterwards the measured quantities, at  $21^{\circ} F.$ , in a water-bath, and ascertaining the amount of solid residue.

The uric acid was determined by treating the salts at a boiling temperature, with strong muriatic acid, allowing the solution to cool, collecting,

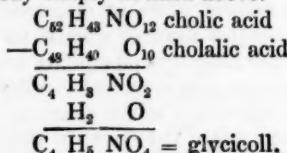
\* Ann. der Chemie und Pharm. Lxv. p. 184.

washing, drying, and weighing the uric acid. This process is sufficiently exact for ascertaining whether a neutral or acid salt is the subject of analysis.

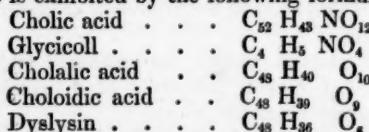
The results obtained with reference to the respective solubility of the urates are of interest, as shewing that the lime-salts will be most calculated to prevent the formation of uric acid calculi : for, the acid urate of lime is the most soluble of the urates, after the alkaline salts, and these cannot well be supposed to exist in the organism, being decomposed by free carbonic acid.

Acid urate of lime is soluble in 623 parts of cold and in 276 parts of boiling water.

*On the resolution of cholic acid into glycicoll and non-nitrogenous acids.\** —In a former communication,† Dr. Strecker observed that cholic acid was converted into cholalic acid and a carbonaceous substance, by boiling alkali, and he now obtains the same result by the use of concentrated barytes-water. After boiling for eight hours, the cholalic acid and the barytes are precipitated by sulphuric acid, the excess of sulphuric acid is removed by hydrated oxide of lead, and the lead again by sulphuretted hydrogen ; on concentrating the liquid, colourless prismatic crystals are obtained, which are identical in composition and properties with glycicoll. The formation of this substance is explained by the separation of cholalic acid from cholic acid, and the assumption of the elements of water by the carbonaceous body simply notified above. Thus :



Glycicoll was also obtained by the action of hydrochloric acid during six hours upon cholic acid, and the resinous bodies which separated at the same time were found to vary in composition by the elimination of the elements of water, in proportion to the length of time which is expended in the process. The choloïdic acid of Demarçay is thus obtained, and as a final product, the dyslysin of Berzelius ; the composition of these successive products is exhibited by the following formulae :



The same products, cholic acid, choloïdic acid, and dyslysin, are obtained by treating the entire ox-bile with acids ; and it is hence obvious that the constituent containing the sulphur of the bile, choleic acid, must possess a similar constitution to cholic acid, with this difference, however, that under the same circumstances, it yields taurine instead of glycicoll.

The constitution of ox-gall is therefore simply explained by supposing it to contain a single non-nitrogenous acid, copulated, if we may so express it, with glycicoll (cholic acid) and with taurin (choleic acid).

THE  
QUARTERLY JOURNAL  
OF THE  
CHEMICAL SOCIETY OF LONDON.

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Nov. 6, 1848.

The President in the Chair.

Dr. Anderson presented to the Library a copy of his papers "On the Colouring Matter of the *Morinda Citrifolia*," and Part I, "On the Products of the Destructive Distillation of Animal Substances."

The following papers were read :

XXVII. *On the composition of Coniine, and its products of decomposition.* By J. BLYTH, M.D., Royal Agricultural College, Cirencester.

It is a disputed point whether the conium of modern botanists is the same as the *κωνεῖον*—the celebrated state poison of the Athenians—and which was also known to the Romans under the name of *Cicuta*. The *Conium maculatum* has at all events been long known as a highly poisonous plant. The investigations hitherto undertaken with it, and its active principle, have been rather of a physiological than of a chemical nature. The poisonous property appears to reside in all parts of the plant, but in greatest abundance in the seeds. Gieseke,\* in 1827, first detected the active principle of conium, without however actually separating it. By distilling the plant with caustic lime and water, he obtained a disagreeably smelling fluid, which after saturation with sulphuric acid, and evaporation, formed with alcohol an extract which possessed all the

\* *Journ. de Pharm.* xiii. p. 366.

poisonous properties of conium in a high degree. Brandes and Gieseke,\* in 1829, gave a method for separating the active principle, on which they bestowed the name of Coniine. Fresh-pounded hemlock was digested for some days with alcohol, the extract evaporated to the consistence of syrup, then softened with water, and finally evaporated to dryness, after mixing it with magnesia, alumina, or oxide of lead. On extracting the dry mass by a mixture of alcohol and ether and evaporating the solution, they obtained the coniine, which is stated to be devoid of all alkaline properties. It is to Geiger† that we are indebted for the actual separation in quantity of coniine, and for an accurate description of its chemical properties.

He obtained it from the ripe and unripe seeds and footstalks by distillation with water, carbonate of potash and hydrate of lime. The distilled fluid was saturated with sulphuric acid, and a volatile oil separated, which accompanied the coniine. After evaporation, the residue was treated with a mixture of three parts of absolute alcohol and one of ether, by which the sulphate of coniine was separated from sulphate of ammonia, produced by the decomposition of the former.

The alcohol and ether were removed by distillation, the residue mixed with water was evaporated to the consistence of syrup, and after the addition of caustic potash, distilled by the heat of a chloride of calcium bath. From six pounds of fresh, and nine of dry seeds, nearly one ounce of oil was obtained, whilst 100 lbs. of the fresh plant gave scarcely one drachm. Christison,‡ who made a thorough investigation of the physiological action of coniine, procured this substance in largest quantity from the unripe seeds, but in the small proportion of two and a half ounces of oil from forty pounds of seeds.

It was a question whether coniine might not, like the volatile oil of bitter almonds, be only a product of decomposition, produced perhaps by the action of the caustic potash. The similar effects produced by the use of the fresh plant and of the oil in the physiological experiments of Christison,§ Orfila|| and Schubartt¶ appeared to remove the doubts on this point, and O. Henry and Boutron-Charlard\*\* afterwards proved, by substituting magnesia in the distillation for that strong alkali, that coniine was not the product of the action of the potash, but really an educt.

\* Journ de Chim. Med. iv. p. 138.

† Mag. für Pharm. xxxv. p. 75 and 259.

‡ Trans. Roy. Soc. Ed. vol. XIII.

§ Loc. cit.

|| Tox. Gen. II. p. 303.

¶ Horn's Archiv. für Med. Erfahr. 1824.

\*\* Journ. de Ch. Med. t. II. 2ème Sér. p. 530.

The analysis by Liebig\* of a portion of the oil prepared by Geiger, gave in one hundred parts :

Carbon	=	66.913
Hydrogen	=	12.000
Nitrogen	=	12.805
Oxygen	=	8.282.

From these numbers, with the atomic weight found by Geiger, (=1406.25), he deduced the formula



Geiger prepared several salts of coniine by mixing directly the acids with the oil, and evaporating in vacuo. He found that they crystallized with difficulty, and were deliquescent in the air. Their chief characteristic appeared to be great instability in solution, undergoing decomposition at ordinary temperatures. By warming and evaporation, decomposition took place much more rapidly. The colour became dark, and this change was accompanied by the separation of brown flakes. The addition of an alkali caused the evolution of ammonia, and the precipitation of coniine, accompanied by a bitter, inodorous, resinous mass, which possessed no poisonous properties. This same brown substance was formed by the action of the air on coniine. More recently, Ortigosa† analyzed coniine, and found that it contained no oxygen. The formula he deduced from the analysis of the platinum-salt was



By the kindness of Dr. Hofmann, of the Royal College of Chemistry, and of Mr. Merck, of Darmstadt, I had specimens of coniine placed at my disposal for analysis, but from the small quantity of material and my inability to procure at present a farther supply, I have been obliged to leave some interesting points uninvestigated, and give the present communication in an incomplete form.

The first specimen, (No. 1), from Dr. Hofmann, was of a pale straw colour, and contained a large quantity of water, which was withdrawn by sticks of caustic potash. Common chloride of calcium of the shops, containing generally alumina, cannot be employed for this purpose. The use of potash, on the other hand, appears to be attended, in some instances, with disadvantage, the reason of which it is difficult to explain. In the specimen, No. 1, the water was withdrawn without any particular effect; whilst in Mr. Merck's,

\* Mag. für Pharm. xxxvi. p. 161.

† Ann. der Ch. und Phar. XLII. p. 313.

(No. 2), the addition of this alkali caused such a violent evolution of ammonia, that the oil was instantly decanted off, to prevent further decomposition. The odour of this portion of oil was also less disagreeable than that of the other. After allowing the No. 1 oil to stand two days over caustic potash, and frequently agitating it, it was decanted and distilled in a current of hydrogen gas, and the distillate collected in separate parts. At 97° C. (207° F.) vapours were abundantly formed, and the temperature rose rapidly to 132° C. (290° F.), when the receiver was changed, the fluid coming over at this temperature being of greater specific gravity. From 132° to 170° C. (290° to 358° F.) the temperature rose more rapidly, the contents of the retort assumed a thick milky appearance, and the last drops of the distilled oil appearing of a denser nature, the receiver was again changed. But little more oil passed over, and the residue contained a considerable portion of potash, which had been held in solution, either by the water mixed with the oil or by the oil itself. Both of these portions were perfectly transparent and colourless. The third quantity, obtained between 170° and 175° C. (358° and 367° F.), was of a light straw colour. The fourth, distilled between 175° and 181° C. (367° and 378° F.), became milky in a corked tube after two days. The fifth portion, passing over between 181° and 219° C. (378° and 446° F.), separated, on standing, into two layers, the upper being of a reddish yellow, the under of a deep red colour, and very thick and viscid. The constant change of the boiling point indicated the presence of some other body besides water, which passes off rapidly with the first portions of coniine. Geiger found that by distilling hemlock with water, a volatile oil was obtained, possessing none of the properties of coniine. It is possible that the presence of some of this oil may be the reason why the boiling point of coniine varied so constantly. The quantity of material in my possession was much too small to attempt a complete separation by distillation. The action of bromine, however, indicated, that with the first portion of oil distilled, a considerable quantity of some other oily body must be present. Bromine forms instantly a crystalline compound with coniine, and the ready formation of these crystals is an approximative method of judging of the purity of the distillate. The first portion of the oil, distilled between 97° and 132° C. (227° and 290° F.), formed with bromine a red fluid, without at first any appearance of crystallization. It was only after long spontaneous evaporation, that a few very indistinct crystals were deposited, evidently formed from the small quantity of coniine which had passed over with the vapour of the other fluid. Both portions of oil, distilled between

132° and 170° C. (290° and 358° F.), and between 170° and 175° C. (358° and 367° F.), instantly crystallized when exposed, a few drops at a time, in a watch-glass to the vapours of bromine. Above 175° C. (367° F.), coniine evidently undergoes decomposition, and with its vapour there likewise distils over a product of decomposition of higher specific gravity and darker colour, which, with bromine, forms a red oily fluid, with only very few indistinct points of crystallization. In consequence of the accompanying impurities, and the great facility of decomposition, the boiling point of coniine could only be ascertained approximatively. For this purpose, the portion of oil which was distilled between 170° and 175° C. (358° and 367° F.), and which solidified instantly into a crystalline mass with bromine, was again submitted to distillation without hydrogen gas. On applying heat, the oil became opalescent at 50° C. (122° F.), and regained its transparency at 65° (149° F.), a small quantity apparently of watery vapour at the same time condensing on the upper part of the retort. Before proceeding further with the distillation, the oil was removed from the retort, and left in contact with pieces of metallic potassium. Violent action ensued, with the evolution of gas and formation of potash. The oil decanted from the latter was then submitted to distillation. Vapours began to form at 70° C. (178° F.), and the thermometer rose rapidly to 168° (335° F.), when it remained stationary for a short time. Between this point and 170° (338° F.), it rose very slowly, and the greatest portion of the oil distilled over. Above 172° (332° F.), decomposition appeared to commence, the boiling point ascended rapidly, and dense white fumes were formed. Between 168° and 171° C. (335° and 350° F.) may therefore be taken as the nearest approximation to the boiling point of coniine. Geiger found it to be 150° C. (302° F.), Christison 188° C. (377° F.), and Ortigosa 212° C. (394° F.).

Cconiine, when first distilled, is a transparent, colourless oil, of spec. gr. 0·878, according to Geiger, 0·89. It is volatile at all temperatures, and its vapours irritate the eyes. It possesses a penetrating, disagreeable odour, which adheres most obstinately to the skin when the oil is brought into contact with it; the hands, when soiled with the oil, continuing on the application of warmth to emit for days a strong odour, resembling that of mice. At ordinary temperatures, coniine retains a portion of water, which causes milkiness on the application of heat. With the vapours of nitric, hydrochloric and acetic acids, it forms dense white fumes. It is quite soluble in alcohol, ether, acetone and oils, but sparingly in the bisulphuret of

carbon. On litmus or turmeric it exerts no action in the anhydrous state, but exhibits the strongest alkaline reaction on the addition of a drop of water. The effect, however, is not permanent. From turmeric, it is immediately dissipated by heat, but from litmus it disappears more slowly, particularly if a strong watery solution of coniine has been employed. It readily coagulates the white of egg. Sulphur is extremely soluble in it, forming with it a dark orange solution, from which the sulphur is again deposited by evaporation in a crystalline form. On phosphorus coniine appears to have no action. Coniine is a much more powerful base than the metallic oxides of the sulphuretted hydrogen and sulphide of ammonium groups. It precipitates copper, lead, zinc, iron, manganese and alumina from their salts, but is without action on the salts of the alkaline earths. From the nitrate of silver it precipitates the oxide, which is very soluble in an excess of the oil. Chloride of silver is as soluble in this base as in ammonia, and is re-precipitated by the addition of nitric acid.

A portion of oil, completely deprived of water, and distilled between  $168^{\circ}$  and  $171^{\circ}$  C. ( $325^{\circ}$  and  $340^{\circ}$  F.), at which the boiling point was most constant, was burnt with oxide of copper and copper turnings.

0·2865 grms. gave  $\text{CO}_2 = 0\cdot789$ ,  $\text{HO} = 0\cdot337$  in 100 parts :

$$\text{Carbon} = 75\cdot11$$

$$\text{Hydrogen} = 13\cdot06$$

Ortigosa obtained in two analyses :

I. 0·199 grm. gave  $\text{CO}_2 = 0\cdot546$  :  $\text{HO} = 0\cdot218$

II. 0·3318 grm. gave  $\text{CO}_2 = 0\cdot904$  :  $\text{HO} = 0\cdot358$

Taking C = 75, these numbers correspond to :

I.	III.
Carbon = 74·83	74·30
Hydrogen = 12·17	11·98

The formula which Ortigosa adopted from his atomic weight, is  $\text{C}_{16} \text{H}_{16} \text{N}$  requiring in 100 parts :

$$\text{Carbon} = 76\cdot19$$

$$\text{Hydrogen} = 12\cdot70$$

The difference between the experimental and theoretical amount of carbon and hydrogen showed that the formula was not quite correct. To control the numbers obtained, the atomic weight was therefore determined anew from the platinum double salt.

Perfectly colourless specimens of coniine were used, as it will be

afterwards seen that if the oil has become coloured by exposure to the air, it is unfit for this purpose. The salt was prepared by neutralizing the oil with hydrochloric acid, adding alcohol and ether, mixing with it an alcoholic solution of bichloride of platinum, and evaporating the mixture in vacuo over sulphuric acid. The crystals were large and of a beautiful scarlet colour. The largest of these were pounded and well washed with alcohol and ether.

- I. 1·2465 grm. gave metallic platinum 0·3635 = 29·16 Pt. per cent.  
 II. A second portion of salt was prepared from the same specimen of oil, and treated in a similar manner. 0·903 grm. gave metallic platinum 0·262 = 29·02 Pt. per cent.

The atomic weight was determined a third time from a totally different specimen of oil obtained from Mr. Merck of Darmstadt. A transparent colourless portion distilled between 160° and 171° C. (320° and 340°) was saturated with strong hydrochloric acid, diluted with water, to which a watery solution of bichloride of platinum was added. By evaporation in vacuo, large red crystals were formed, similar to those from the alcoholic solution. The large crystals, which had united into a thick cake, were pounded and washed as before, and dried in an air-bath at 50° to 55° C. (122° to 131° F.), and finally in the water-bath between 83° and 86° C. (182° and 187° F.)

- III. 0·810 grm. gave metallic platinum 0·2355 = 29·07 Pt. per cent.

The atomic weights of the double salt, calculated from these three analyses, is :

I.	II.	III.	Mean.
4230·1	4250·5	4243·2	4241·2

The atomic weight of coniine will, therefore, be 1664, and the formula calculated from the analysis of the oil :



which gives in one hundred parts :

Calculated.	Found.
Carbon = 76·66	75·11
Hydrogen = 12·78	13·06
Nitrogen = 10·52	

The deficiency found in the carbon is partly due to the decomposition which coniine undergoes when submitted to distillation, a portion being probably left in the bulb in a resinous non-volatile form. The more probable source of error, however, seems to lie in the admixture of some other oily body, which is shown by the constant change of the boiling point. The control for the formula was,

therefore, sought in the analysis of some compound which could be more completely burned, and could be obtained of greater purity than the oil. Here again a difficulty presented itself in the deliquescent nature of most of the salts of coniine, which rendered them unfit for such a purpose. The small quantity of material in my possession, likewise, obliged me to limit my investigations to the most stable compounds, trusting to correct the formula by the products of decomposition.

#### COMPOUNDS OF CONIINE.

*Action of Chlorine.*—On bringing coniine in contact with chlorine gas, dense white fumes are formed, possessing in some degree the odour of the oil of lemons. On passing the gas into a portion of oil, distilled about  $130^{\circ}$  C. ( $266^{\circ}$  F.), the temperature is suddenly raised very high, and the colour becomes of a dark red. A large quantity of very dense white fumes are at the same time evolved. On plunging the tube into cold water, to prevent too rapid action, and continuing the transmission of the gas, the oil again becomes colourless, and gradually increases in consistency, the evolution of the white fumes ceasing at the same time. The upper portion of the tube becomes covered with a white crystalline substance, but the oil must be long submitted to the action of the gas before it is entirely transformed into a crystalline mass.

In its crystalline form, the chlorine compound resembles the corresponding one of bromine, and is very soluble in alcohol and ether, from which it is deposited in a crystalline form. It is likewise very soluble in water, on the surface of which it performs a violent, jerking, rotatory motion. It is a very volatile compound.

*Action of Bromine.*—The formation of the bromine compound with pure coniine is attended with no difficulty. If too large a quantity of bromine be employed, or the oil obtained at a lower temperature than  $168^{\circ}$  C. ( $335^{\circ}$  F.) be used, the chief product is either a gummy mass in the one case, or a red fluid in the other. Bromine is a good test for the quantity of coniine present in each of the fractional distillates. If a small quantity of pure oil, distilled at  $169^{\circ}$  C. ( $336^{\circ}$  F.), be placed on a watch-glass and exposed to the vapours of bromine, it instantly solidifies into a crystalline mass of needles. The first portions of oil obtained between  $98^{\circ}$  and  $136^{\circ}$  C. ( $209^{\circ}$  and  $276.5^{\circ}$  F.), exhibit, at first, no appearance of crystallization, and by evaporation in vacuo, become dark red in colour.

A portion of coniine, distilled between  $98^{\circ}$  and  $132^{\circ}$  C. ( $209^{\circ}$  and  $270^{\circ}$  F.), was mixed with bromine and left for twenty-four hours over

sulphuric acid, in vacuo. It became black from the excessive action of bromine. The dark mass was dissolved in water, boiled for a short time with animal charcoal, filtered, and again evaporated in vacuo. Long, transparent, colourless crystals were deposited from the concentrated solution. The mother-liquor undergoes decomposition, with the formation of the same product as is observed in slowly evaporating the solution of the sulphate at a gentle heat.

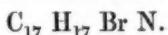
This compound is very soluble in alcohol and water, but much less soluble in ether, by which it can be purified. From the alcoholic and watery solutions, it again separates by slow evaporation almost to dryness, in radiating needles. It does not deliquesce on exposure to the air. It melts, a little above  $100^{\circ}$  C. ( $212^{\circ}$  F.), to an oily fluid with slight evolution of the vapours of coniine, and solidifies again on cooling to a mass of radiated needles. The largest crystals, powdered and well washed with ether, were analysed with chromate of lead and metallic copper.

I. 0.3755 grm. gave  $\text{CO}_2 = 0.6680 : \text{HO} = 0.3055$ .

In 100 parts :

Found.	Calculated.
Carbon = 48.52	48.28
Hydrogen = 8.98	7.57

The formula calculated from the above is :



*Action of Iodine.*—A weak alcoholic solution of iodine was added to a portion of oil, dissolved likewise in alcohol. On the addition of each drop of the solution, a dark brown precipitate took place, which dissolved to a colourless fluid. If so much iodine has been added as to leave the solution coloured, a considerable portion of the oil is decomposed on evaporation in vacuo. The mother-liquor is in every case brownish. The compound resembles, in crystalline form, the similar one of bromine. It is very soluble in alcohol, water and ether.

*Salts of Coniine.*—Few of the salts of coniine can be well characterized by description. Many of them, when evaporated to crystallize, undergo decomposition and leave gummy masses. A few crystallize, but are so deliquescent as to render them unfit for analysis.

*Hydrochlorate of Coniine.*—A portion of the No. 2 oil, distilled between  $160^{\circ}$  and  $171^{\circ}$  C. ( $320^{\circ}$  and  $340^{\circ}$  F.), was saturated with strong hydrochloric acid. The fluid, which was at first colourless, became of a faint red tint after saturation. The hydrochlorate is so extremely soluble, that it requires to be evaporated almost to

dryness before it indicates any symptoms of crystallization. From a very concentrated solution, long white crystals shoot out in a stellated form. They cannot be exposed to the air, as they immediately deliquesce.

*Sulphate of Coniine.*—A portion of oil, saturated with dilute sulphuric acid, was evaporated on the water-bath. The solution became of a brownish colour as the evaporation proceeded, and finally left a thick gummy mass, in which there were indistinct indications of crystallization. By the addition of caustic potash, the oil was again separated, with its characteristic odour. If the evaporation be pushed a little further, decomposition takes place, with the production of the same substance as in the case of bromine already mentioned.

*Double salt of Coniine and Platinum.*—A portion of oil, distilled between  $106^{\circ}$  and  $136^{\circ}$  C. ( $223^{\circ}$  and  $275\cdot5^{\circ}$  F.), was neutralized with hydrochloric acid and mixed with alcohol, and to the mixture an alcoholic solution of bichloride of platinum was added. The fluid assumed a dark red, oily appearance, but no precipitate took place. By evaporation in vacuo, the double salt was deposited in tufts, of a deep red colour. The mother-liquor, on further evaporation, deposited no more crystals, but evolved much hydrochloric acid. An abundant crop of large and well formed crystals may, however, be obtained, by the addition of water, and further evaporation over sulphuric acid.

To prepare this salt, perfectly colourless coniine must be employed. By using a coloured oil, the red salt is invariably mixed with a dark substance, from which it is impossible to separate it. When crystallized from a weak alcoholic solution, over sulphuric acid in vacuo, the crystals unite into solid cakes, of a deep red colour.

Their form is that of a regular four-sided prism, truncated or terminated by a regular four-sided pyramid. This salt is sparingly soluble in cold ether, alcohol and water, but readily soluble in boiling alcohol, from which it is again deposited in a crystalline form. It can be heated without decomposition, in the water-bath, to  $100^{\circ}$  C. ( $212^{\circ}$  F.), but on raising the temperature a few degrees beyond this point, it fuses, and evolves fumes of coniine. By the addition of potash, it is decomposed without the application of heat.

I. 0·446 grm. burned with chromate of lead and metallic copper, gave  $\text{CO}_2 = 0\cdot4885$ ,  $\text{HO} = 0\cdot2165$ .

II. 0·512 grm. prepared from a different specimen, and burned in the same manner, gave  $\text{CO}_2 = 0\cdot555$ ,  $\text{HO} = 0\cdot227$ .

III. 0·7785 grm. analyzed by Varrentrapp and Will's method,

gave 0·507 of the double salt of platinum and ammonium, = 4·05 nitrogen per cent.

These numbers correspond in 100 parts to :

	I.	II.	III.
Carbon	= 29·87	29·56	
Hydrogen	= 5·39	4·92	
Nitrogen	=		4·05

The formula of the double salt, taken from the above analyses and the preceding atomic weight, is :



which gives :

	Calculated.	Mean. of experiments.
C <sub>17</sub> = 1275	30·07	29·77
H <sub>18</sub> = 225	5·30	5·16
N = 175	4·12	4·05
Pt = 1233·5	29·09	29·08
Cl <sub>3</sub> = 1331·25	31·39	—
<hr/>		
	4239·75	

The mean atomic weight of the double salt found, was 4241·2.

*Compound of Coniine and Chloride of Mercury.*—A portion of oil, distilled between 147° and 160° C. (297° and 320° F.), and which had become brown on exposure to the air, was re-distilled. A clear oil passed over, leaving a dark resinous mass in the retort. The distillate was dissolved in alcohol, and an alcoholic solution of chloride of mercury added to it. An abundant precipitate took place, which on stirring, collected at the bottom of the vessel, in the form of a viscid substance, of a pale lemon colour. It is insoluble in water and ether, and very sparingly soluble in alcohol. It is quite soluble in hydrochloric acid, from which it is deposited by evaporation as a gummy mass. It preserves its viscid character when exposed to the air, but if placed for some time in ether, it gradually hardens, and can then be pounded. The pounded substance was purified by washing with ether and water. The powder is of a pale lemon colour, and undergoes decomposition with the greatest facility. On exposure to the temperature of 32° C. (90° F.), it evolves the odour of coniine, which is also perceptible even on evaporation in vacuo over sulphuric acid. At 100° C. (212° F.) it fuses into a hard body, and suffers decomposition.

I. 0·458 grm. gave carbonic acid 0·258.

II. 0·558 grm. dissolved in nitric acid and precipitated by nitrate of silver, gave 0·430 chloride of silver.

A second portion of the compound was prepared from fresh oil, distilled at 169°, by adding a watery solution of chloride of mercury to an alcoholic solution of the oil. By allowing the precipitate to fall without stirring, it was deposited as a pale lemon-coloured powder, having none of the appearance of the former viscid substance.

III. 0·5585 grm. gave  $\text{CO}_2=0\cdot334$ ,  $\text{HO}=0\cdot135$ ,  $\text{Hg}=0\cdot337$ .

The mercury was collected in this analysis by contracting the combustion-tube where the metallic copper terminated, and filling eight inches of the remaining portion with asbestos. The water was separated from the mercury by a current of dry air, warmed to 16° C. (61° F.) Binoxide of nitrogen was formed in this analysis.

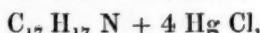
IV. 0·507 grm. decomposed by lime in a tube, gave  $\text{Hg}=0\cdot300$ .

The residue dissolved in dilute nitric acid, and precipitated by nitrate of silver, gave  $\text{Ag Cl}=0\cdot384$ .

These numbers afford in 100 parts :

	I.	II.	III.	IV.
Carbon	= 15·36	—	16·30	—
Hydrogen	= —	—	2·68	—
Nitrogen	= —	—	—	—
Mercury	= —	—	60·34	59·17
Chlorine	= —	19·17	—	18·73

From which may be deduced the formula :



which corresponds in one hundred parts to :

Carbon	= 15·11
Hydrogen	= 2·52
Nitrogen	= 2·08
Mercury	= 59·25
Chlorine	= 21·03

This compound is formed by the direct union of coniine with the mercury salt, and resembles in its constitution the corresponding compounds of nicotine,\* aniline,† and thiosinnamine,‡ and like the latter substance, unites with 4 equivalents of the chloride.

#### PRODUCTS OF DECOMPOSITION OF CONIINE.

*Action of Oxygen.*—The contradictory statements given by medical men of the action of the extract of hemlock, is a sufficient evidence of the unstable nature of its active principle. As much as 2 drachms

\* An. der Ch. und Ph. xli. p. 114.

† Ibid. xlvi. p. 63.

‡ Ibid. lii. p. 14.

to one ounce have been given, in some cases, without effect, whilst a smaller quantity of another extract, prepared in a similar manner, has proved a most powerful poison.\* Christison ascribes this to two causes, viz. to the decomposition of the active principle (coniine) of the extract which takes place on evaporation, and is evidenced by the abundant disengagement of ammonia, and secondly, by the lengthened action of the air, which renders even the best prepared extracts at length quite inert. The truth of this last supposition is easily seen by allowing free access of air to coniine. When first distilled, the oil is quite colourless, but does not long remain so, except in perfectly full bottles. If the vessel contains much air, the colour changes to a light brown, then reddish dark brown, and finally the oil is converted into a nearly black resinous mass. On distilling coniine, with access of air, a portion of this substance is generally left in the retort, the quantity depending on the length of time the oil has been exposed to the action of the air, which may be readily known by its altered colour. A portion of coniine was exposed for four weeks, in a broad shallow basin, to the action of oxygen gas under a bell-glass, the gas being renewed during that period. It became of a dark red colour and gradually thicker in consistence, until it was converted into a soft resinous mass, which could be drawn out in threads. It possessed a strong odour of coniine, and acted strongly alkaline. To free it from undecomposed oil, it was dissolved in strong hydrochloric acid, in which it is very soluble, and precipitated by carbonate of potash. By repeating the operation, and washing with water, the resin was obtained quite pure. The filtrate possessed the odour of coniine.

When freshly precipitated from a moderately strong solution, the resin is of a brick-dust colour, and of a gelatinous consistency. From concentrated solutions it separates as a viscid black substance, like the original resin. When well washed, it no longer possesses the odour of coniine, but on exposure to the air in a wet state, it emits a faint odour of butyric acid, which is rendered more apparent by the application of a gentle heat. It burns with a smoky flame, evolving vapours which have not the least trace of the odour of coniine, but faintly that of butyric acid. All the compounds of coniine, on the other hand, on being burned, evolve the disagreeable irritating vapours of this substance, which continue to pervade the laboratory for some days. The resin is slightly soluble in water, but the solution does not appear to possess either

\* Orfila's *Tox. Gen.* II. 305.

an alkaline or acid reaction. It is also slightly soluble in ether, and very soluble in alcohol, the latter solution being rendered turbid by the addition of water. This substance appears to possess feeble basic properties. Turmeric paper, left in contact with the moist resin for some time, assumes a faint brown tint. It dissolves readily in hydrochloric acid, forming a nearly black solution, and is reprecipitated by the addition of an alkali. It contains nitrogen apparently to the same amount with coniine, as ammonia is abundantly evolved by heating it with soda-lime.

On adding chloride of mercury dissolved in alcohol to an alcoholic solution of the resin, brown gelatinous flakes are immediately precipitated. An alcoholic solution of bichloride of platinum, added to a similar solution of the resin acidulated with hydrochloric acid, produces no effect ; but on evaporating under the air-pump, brown flakes are deposited, mingled with a few white crystals, surrounded by a dark, nearly black mother-liquor, which possesses a faint odour of butyric acid.

This resinous matter forms the connecting link between coniine and its most common product of decomposition, viz. butyric acid, being first converted into this substance before it undergoes its final transformation. On boiling coniine with nitric acid, for the formation of butyric acid, it was found that after the action had continued for some time, potash no longer precipitated the oil from the contents of the retort, but the brown flakes of the resin.

*Action of bichloride of platinum.*—The red-coloured oil no longer gives the beautiful red crystalline compound with bichloride of platinum, but a black crystalline substance. On adding hydrochloric acid to a portion of oil, distilled between  $160^{\circ}$  and  $170^{\circ}$  C. ( $320^{\circ}$  and  $338^{\circ}$  F.), and which had become red by exposure to the air, the colour of the mixture was at first rose, but immediately changed to a brownish green, and finally a dirty brown. Mixed with bichloride of platinum, and evaporated in vacuo, the fluid deposits black crystals, mixed with a small quantity of the red platinum-salt. Along with these were also observed white silky crystals, the amount of which was too small to admit of their nature being investigated. The mother-liquor, on further evaporation, yielded a second crop of the black crystalline compound, surrounded by a dark viscid fluid, which became brown, and deposited flakes on the addition of water. The black crystals were powdered and washed with alcohol.

0·604 5grm. gave metallic platinum 0·184 = 30·43 per cent of platinum. The red salt from the colourless oil contains 29·08 per cent of platinum. On adding potash, the odour of coniine was evolved,

which showed that the substance was a mixture of undecomposed red salt with a new body, which, however, could not be separated.

From the mother-liquor of the red salt, the odour of butyric acid was evolved by long evaporation over sulphuric acid. This being evidently due to an oxidizing action of the bichloride, and similar to that produced on narcotine, it was supposed that a corresponding decomposition of coniine might take place, giving rise to an acid and the platinum-salt of a new base, with or without the evolution of carbonic acid. This supposition was confirmed by experiment. A portion of the double salt of coniine and platinum was placed, with excess of bichloride of platinum, in a flask provided with a long upright tube, connected with a vessel containing lime-water. On boiling the mixture for a short time, the colour became much darker, and carbonic acid was evolved. At the commencement of the process of oxidation, the lime-water bottle was filled with the odour of some fatty substance. As the oxidation proceeded, this was replaced by that of butyric acid. By continuous boiling, the greater part of the bichloride was completely reduced to the metallic state. Towards the end of the operation, the odour of butyric acid was again replaced by that of the fatty substance. At the same time, a small quantity of an oily looking body appeared floating on the surface of the distilled fluid, which on cooling became semi-solid. The quantity was not at all sufficient to admit of its nature being investigated, the small amount of coniine at my command obliging me to reserve it for other purposes. It would therefore be a point of some interest to ascertain the constitution of this body by acting on a larger portion of oil at a high temperature (probably under pressure) with a very feeble oxidizing agent, as this substance appears at a period of the operation, when by the reduction of the greater part of the oxidizing agent, the bichloride of platinum, but a limited supply of oxygen could be obtained.

After continuous boiling for about four weeks, and finally evaporating to dryness, the dark residue was boiled with water, filtered from the reduced platinum, and again evaporated to dryness. The residue was found to consist chiefly of yellow octohedral crystals—long, purple, regular four-sided prisms—and white silky needles, similar to those which had been observed to accompany the black platinum compound. With these were observed a few crystals of the undecomposed coniine and platinum-salt. The white crystals appeared to be of an acid nature, as they were readily dissolved by potash and re-precipitated by hydrochloric acid. The mixed crystals were treated with very dilute cold potash, and rapidly filtered

and washed with water, by which the purple and white crystals were separated from the octohedral. On burning a portion of the latter on platinum foil, metallic platinum was left without *any previous carbonization*. On heating them in a tube with caustic lime, they evolve ammonia abundantly. This substance was therefore the double salt of platinum and ammonium, derived from the nitrogen of the coniine by its complete decomposition. The percentage of platinum could not be accurately ascertained, in consequence of the presence of a small quantity of the double salt of potassium and platinum, formed by the decomposition of the few crystals of the coniine double salt, by means of the dilute potash employed to separate the mixed substances. The filtrate from the octohedral crystals was of a purple colour, and, on evaporation to dryness, deposited the long, regular, four-sided prisms, mixed with the white crystals. The purple substance being found to be insoluble in alcohol, in which the white crystals readily dissolved, that liquid afforded an easy method of separating the two. On dissolving the two bodies in water, and adding alcohol to the purple solution, long purple crystals were deposited, leaving the mother-liquor colourless. They were thrown on a filter and washed with alcohol. On drying the filter with the precipitate at  $100^{\circ}$  C. ( $212^{\circ}$  F.), decomposition took place, with deposition of metallic platinum. This reaction being due to the alcohol present, the remainder was quickly dissolved in water, and evaporated slowly to dryness, when the long purple crystals were again formed. They are very soluble in water, but insoluble in alcohol and ether. On heating a portion on platinum foil, it left metallic platinum *without previous carbonization*. Heated with caustic lime, no evolution of ammonia took place. In all its properties this substance resembled the compound of chloride of potassium and protochloride of platinum described by Magnus.\* On decomposing the salt by heat, and dissolving out the chloride of potassium, 43 per cent of metallic platinum was left; the protochloride of platinum and potassium contains 47 per cent. The difference here evidently arose from the small quantity of salt analyzed. The purple crystals first obtained by evaporating to dryness the filtrate from the coniine and platinum double salt, which had been long boiled, must have been a similar compound of protochloride of platinum and ammonium, also described by Magnus.† In endeavouring to separate the mixed crystals by dilute caustic potash, this salt had undergone decomposition, with the formation

\* Pogg. An. xiv. s. 241.

† Loc. cit.

of the corresponding potassium compound. The latter could not have been formed by the potash with any free protochloride of platinum which may have been supposed to be present, as this chloride is insoluble in water, and could only have been present in solution either in hydrochloric acid or bichloride of platinum. The former was driven off by the first evaporation to dryness, and not only had the excess of bichloride of platinum employed undergone complete decomposition, but the bichloride likewise in combination, by contributing to the oxidising action, was likewise reduced. To ascertain this point, a portion of fine crystals of the red platinum-salt of coniine, perfectly free from bichloride of platinum was enclosed in a strong tube with a small quantity of water. On submitting it for a short time to a heat of  $140^{\circ}$  C. ( $284^{\circ}$  F.), it first dissolved, then gradually became of a darker colour, and finally deposited a black substance. The black matter was metallic platinum. The filtrate from the platinum was of a pale brown colour, and of an agreeable aromatic odour. It deposited no crystals until evaporated nearly to dryness. On adding caustic potash, the odour of coniine was evolved, but no crystals of bichloride of platinum and potassium were formed, the bichloride of platinum having been evidently reduced to the state of protochloride in combination with the coniine. The coniine compound has no resemblance to the purple crystals; and as the latter were deposited on the first evaporation before the addition of caustic potash, they must have been the ammonium-salt analogous to that of potassium, afterwards obtained.

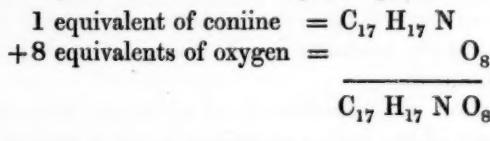
The formation of protochloride of platinum and ammonium as a final product of the action of bichloride of platinum on coniine, is not peculiar to this oil. It is probable that it is formed in every case in which an alkaloid is completely decomposed by this reagent. On a former occasion, on submitting the narcotine double salt to continuous boiling with this substance, alcohol precipitated from the deep purple mother-liquor crystals exactly resembling those above described, the nature of which however was not ascertained, in consequence of their complete decomposition, with deposition of metallic platinum, on the application of a gentle heat to the alcoholic mixture.

#### BUTYRIC ACID.

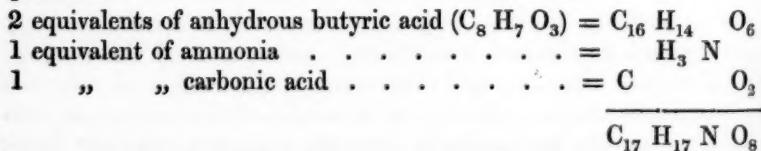
This is one of the most common products of decomposition of coniine by all oxydizing agents. By the simple evaporation in vacuo of the bromine compound, with slight excess of bromine, it is pro-

duced when the fluid becomes concentrated. Its odour is also detected when the sulphate is evaporated to a gummy consistency over a spirit-lamp, at a gentle heat. It is readily obtained by distilling coniine with strong nitric acid. To avoid the difficulty of separating the nitric acid, chromic acid was employed as the oxidizing agent. A quantity of the oil was exposed for a week, without the aid of heat, to the action of bichromate of potash and sulphuric acid, when the formation of butyric acid rapidly took place. The mixture was finally submitted to repeated distillation to oxidize any undecomposed oil. The distillate reacted strongly acid, and possessed in a high degree the characteristic odour of butyric acid. The nature of the distillate was sufficiently characterized by the following reactions. Mixed with potash and evaporated to dryness, the compound crystallized in cauliflower-looking masses which were highly deliquescent. The baryta-salt formed by decomposing the potash compound with chloride of barium, evaporating to dryness and extracting with alcohol, crystallized from this solution in long prisms, which when thrown on water, exhibited the characteristic rotatory motion of the butyrate of baryta. Finally, on adding to the distillate sulphuric acid and alcohol, the mixture became hot, with the immediate separation of butyric ether, possessing its aromatic pine-apple odour.

On comparing the products of decomposition with the preceding analyses, the composition of coniine may be represented as follows :



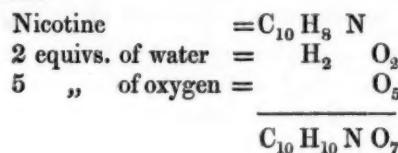
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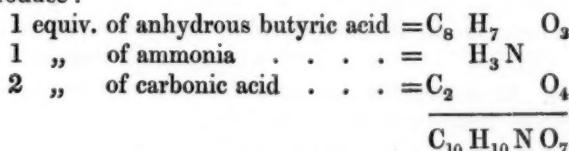
In the dry distillation of tobacco, Zeise\* observed, among other products, a reddish fluid, which, on further distillation with sulphuric acid, gave butyric acid. The active principle of tobacco (nicotine) being an oily nitrogenized body, similar in its nature to coniine, it is possible that, like the latter, the butyric acid was derived from its decomposition. In such a case, it was probable that some close relation might have been shown to exist between these two peculiar alkaloids.

\* An. der Ch. und Phar. XLVII. 215.

By adding 5 equivalents of oxygen and 2 of water to nicotine, the elements of products of decomposition are obtained, similar to those derived from coniine.



would produce :



As yet, however, I have not been able to effect this decomposition of nicotine.

By decomposition *under pressure*, the platinum-salt of coniine gives rise to a white crystalline compound, which I must reserve for further investigation, when I have been able to procure a fresh portion of the oil.

This method of treating the platinum double salt of the alkaloids, with, at the same time, excess of bichloride of platinum, appears to transform readily into new compounds those which have as yet been submitted to experiment. I am at present engaged with the prosecution of this subject.

**XXVIII.—Observations on the Atomic Volumes and Boiling Points of analogous Organic Liquids. By W. A. MILLER, M.D., F.R.S., Professor of Chemistry at King's College, London.**

It is well known that Kopp,\* from a series of researches and observations on the atomic volume and the boiling points of various organic liquids, some years ago, deduced the conclusion that analogous fluid compounds exhibit like differences in their equivalent volume. That the atomic volume of a hydrated acid, for example, is about 534 less than that of the corresponding ether, and about 300 less than that of the corresponding methyl compound; whilst between corresponding compounds of the ethyl and methyl series, there is a difference equal to about 234 in the atomic volumes of the two.

\* Annalen der Chemie, 1841. Bd. 41, s. 79.

Between the boiling points of the hydrated acids and the ethers he finds a difference of . . . . .	45°
Between the acids and the methyl compounds . . . . .	63°
And between the corresponding ethyl and methyl compounds . .	18°

Later experiments and observations led him to the conclusion, that two members of the ethyl and methyl series of compounds, which differ in their empirical atomic formulæ by multiples of (2 CH), differ by equal multiples of 19° C. in their boiling points.\*

He has further concluded, that the atomic volume of an element, in all fluid compounds, at corresponding temperatures, is the same, and that chemical equivalents of oxygen and hydrogen in fluid compounds, at corresponding temperatures, occupy equal bulks. Corresponding temperatures being understood to be those at which the tension of vapour of the two is equal. In default of observations on the equal tension of the vapours, Dr. Kopp has assumed as approximations to the truth—temperatures equidistant from the boiling point as “corresponding temperatures.”

In this country, the attention of chemists generally has lately been recalled to this theory by the appearance of a valuable report on the subject in the 1st volume of the Cavendish Society’s publications, and the following remarks may, therefore, not be without interest. M. Pierre,† having recently published a series of most elaborate researches upon the expansion of a considerable number of liquids, both inorganic and organic, and having with great care determined their boiling points, and their specific gravities at 0° C., I was induced, in order to satisfy myself of the correctness of the generalizations of Kopp, to test them by the new data thus furnished. To my great surprise, however, and disappointment, I may add, I found the results very wide of those required, if the views entertained by Kopp be correct; and it may be worth while, in the present period of the discussion, simply to state them.

The laborious researches of M. Pierre have embraced no fewer than twenty-eight liquids, some inorganic, others organic compounds. Twelve of these will serve directly for the purposes of the present inquiry.

The following table includes the results observed by M. Pierre.

It may here be mentioned, that these experiments prove, as indeed Kopp had surmised it to be probable, that similar compounds do not expand equally at equal distances from the boiling point, and this

\* Annalen der Chemie, Bd. 55, s. 177.

† Annales de Chimie and de Physique 3ème Série, Vol. xv. p. 325, xix. p. 193, xx. p. 5.

variation necessarily introduces some discrepancy between Kopp's calculated results and those furnished by experiment. The observations of Pierre, moreover, enable us to obviate this objection by calculating the atomic volume not at equal distances from the boiling point, but at the boiling point itself, *i. e.*, just as the cohesion of the liquid is about to yield. This calculation I have accordingly made.

TABLE I.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Name.	Formula.	Equi- valent.	Boiling point C°. =	1000 at 0° at boiling.	Sp. gr. 0° C.	At boil- ing.	At boiling point. Atomic volume.
Fouzel oil . . .	C <sub>10</sub> H <sub>11</sub> O, HO	1100	131.8	1153	0.827	0.717	1534.5
Alcohol . . .	C <sub>4</sub> H <sub>9</sub> O, HO	575	78.3	1093	0.815	0.745	771.0
Wood-spirit . . .	C <sub>2</sub> H <sub>5</sub> O, HO	400	66.3	1089	0.820	0.754	530.0
Iodide of ethyl . . .	C <sub>4</sub> H <sub>9</sub> , I	1942	70.	1088	1.975	1.815	1070.0
Iodide of methyl . . .	C <sub>2</sub> H <sub>5</sub> , I	1767.0	43.8	1058	2.199	2.076	851.0
Bromide of ethyl . . .	C <sub>4</sub> H <sub>9</sub> , Br.	1340.8	40.7	1059	1.473	1.391	964
Brom. of methyl . . .	C <sub>2</sub> H <sub>5</sub> , Br.	1165.8	13.0	1019	1.664	1.633	714
Acetate of ethyl . . .	C <sub>4</sub> H <sub>9</sub> O, C <sub>2</sub> H <sub>5</sub> O <sub>3</sub>	1100	74.14	1110	0.907	0.817	1346
Acetate of methyl . . .	C <sub>2</sub> H <sub>5</sub> O, C <sub>2</sub> H <sub>5</sub> O <sub>3</sub>	925	59.5	1088	0.866	0.796	1162
Butyrate of ethyl . . .	C <sub>4</sub> H <sub>9</sub> O, C <sub>4</sub> H <sub>9</sub> O <sub>3</sub>	1450	119.0	1171	0.902	0.769	1884
Butyr. of methyl . . .	C <sub>2</sub> H <sub>5</sub> O, C <sub>6</sub> H <sub>5</sub> O <sub>3</sub>	1275	102.1	1147	1.029	0.897	1423
Formiate of ethyl . . .	C <sub>4</sub> H <sub>9</sub> O, C <sub>2</sub> H <sub>5</sub> O <sub>3</sub>	950	52.9	1079	0.935	0.866	1096
Ether . . . .	C <sub>4</sub> H <sub>8</sub> O	462.5	35.5	1057	0.735	0.694	665.8
Water . . . .	HO	112.5	100.0	1044	0.958	0.958	117.4

The headings of the columns of the preceding table will sufficiently explain their contents. Column 5 represents the bulk that 1,000 parts of the different liquids, measured at 0° C., attain when raised to the temperature at which they respectively boil. Column 7, the sp. grav. at the boiling point, being calculated from the data contained in 5 and 6.

TABLE II.

I.	II.	III.	IV.	V.
	Observed difference of		Calculated for each (C <sub>2</sub> H <sub>2</sub> ) difference of	
	Boiling point C°.	Atomic volume.	Boiling point.	Atomic volume.
EO, HO — MeO, HO = C <sub>2</sub> H <sub>2</sub>	..	..	12.0	241
EI — MeI = C <sub>2</sub> H <sub>2</sub>	..	..	26.2	219
EBr — MeBr = C <sub>2</sub> H <sub>2</sub>	..	..	27.7	250
EO, Ac — MeO, Ac = C <sub>2</sub> H <sub>2</sub>	..	..	15.64	184
EO, Bu — MeO, Bu = C <sub>2</sub> H <sub>2</sub>	..	..	16.9	461
EO, Ac — EO, Fo = C <sub>2</sub> H <sub>2</sub>	..	..	21.24	250
MeO, Bu — EO, Ac = C <sub>2</sub> H <sub>2</sub>	..	..	27.9	87
EO, Bu — EO, Ac = 2(C <sub>2</sub> H <sub>2</sub> )	34.8	338	17.43	169
MeO, Bu — MeO, Ac = 2(C <sub>2</sub> H <sub>2</sub> )	42.6	261	21.3	130.5
MeO, Bu — MeO, Fo = 2(C <sub>2</sub> H <sub>2</sub> )	49.2	327	24.6	163.5
EO, Bu — EO, Fo = 3(C <sub>2</sub> H <sub>2</sub> )	66.1	788	22.03	262.6
EO, Bu — MeO, Ac = 3(C <sub>2</sub> H <sub>2</sub> )	59.5	722	19.8	240.7
AmO, HO — EO, HO = 3(C <sub>2</sub> H <sub>2</sub> )	53.5	763	17.8	254.3
AmO, HO — MeO, HO = 4(C <sub>2</sub> H <sub>2</sub> )	65.5	1004.5	16.3	251.1
MeO, Ac — EO, Fo 0	6.6	66	..	..

In this second table, the different compounds enumerated in the first are compared together, two and two. In the first seven cases, the difference between the compounds compared is 1 equivalent of the carbo-hydrogen (C<sub>2</sub>H<sub>2</sub>). In the first five, the difference is in the basic portion of the compound; in the 6th, it is the acid member of each compound; and in the 7th, the difference is in the empirical formula; in the subsequent cases there are differences, of 2 (C<sub>2</sub>H<sub>2</sub>), 3 (C<sub>2</sub>H<sub>2</sub>), and 4 (C<sub>2</sub>H<sub>2</sub>), in all varieties; the last two columns are calculated from the preceding two, by division of the numbers in columns 2 and 3, by the multiple of the carbo-hydrogen which these numbers represent.

In atomic volume the results do not very greatly differ from similar calculations made by Löwig upon the same subject, on data existing previous to the experiments of Pierre.

The difference between alcohol and wood-spirit is . . . . .	241
Between fousel oil and alcohol . . . . .	254·3
"    fousel oil and wood-spirit . . . . .	251·1
The equivalent volume of C <sub>2</sub> H <sub>2</sub> , deduced from these combinations, will be therefore 249 as a mean.	

And with this the conclusion derivable from the bromides of ethyl and methyl . . . . .	=250
And the acetate and formiate of methyl . . . . .	=250

also agree.  
That derivable from the butyrate and formiate of ethyl .262·6  
and the butyrate of ethyl and acetate of methyl . . . . =240·7  
does not greatly differ from the preceding, the mean being 251·6

But here all further agreement with Kopp's law ceases.	
Compare the iodides of ethyl and methyl . . . . .	219
Or the corresponding acetates . . . . .	184
The butyrates corresponding . . . . .	461
The butyrate and acetate of ethyl . . . . .	169
Butyrate and acetate of methyl . . . . .	130
Butyrate of methyl and formiate of ethyl . . . . .	163

or even the formiate of ethyl with the acetate of methyl, two bodies possessing the same empirical formula: we have here a difference of 66 in the atomic volume of the two, instead of perfect coincidence.

It is unnecessary for me to continue further the comparison with other bodies, or deduce the atomic volume of water in combination, from different compounds. Löwig has already shown that Kopp's hypothesis of the equality in volume of oxygen and hydrogen does not correspond with facts, and the new data do not at all affect this general conclusion.

Before any general law can be deduced, with even tolerable hopes of success, a large number of careful and laborious experiments, such as those which have furnished materials for the preceding remarks, are indispensably requisite. The industry of chemists is daily, in some degree, filling up this void, and no one has attempted to remove this difficulty with greater earnestness than Kopp himself; but until this want is supplied, the foundation on which alone such speculations can be built, or on which the still more extended and elaborate calculations of Löwig can be based, is wanting. Numerous remarkable numerical coincidences, in compounds of analogous composition, show that some important quantitative connection between chemical composition and atomic volume exists; but the true law of that connection still remains to be discovered.

Simple inspection of the differences in the volume of the boiling points, where discrepancies exist even still greater than those observed between the atomic volume (differences both in excess and in deficiency far greater than can be attributed to errors of observation), shews the law of Kopp, regarding the boiling points, to be at variance with the facts observed.

**XXIX.—*Researches on the Amyl Series.* By HENRY MEDLOCK, Esq.**

Since the chemical nature of fousel oil, and its interesting relation to various other bodies, was first pointed out by the investigations of Dumas\* and Cahours,† this compound has been the subject of a great number of researches. Balard,‡ Krutzsch,§ H. Kopp,|| Kolbe,¶ Riecker,\*\* and various other chemists, have been successively engaged in its study; and it is to their labours that we are indebted for the knowledge of a considerable number of the derivatives of this important alcohol. Still, this series exhibits by no means the completeness which the corresponding methyl, and particularly the ethyl series, presents to us.

It was with the intention of filling up some of the existing blanks, that Dr. Hofmann invited me to undertake the examination of several of the derivatives of fousel oil.

It was my wish to have brought this investigation before the Society in a more complete form, but seeing in a recent number of the "Journal de Pharmacie"†† that M. O. Henry has announced an investigation in a similar direction, I hasten, in order to avoid collision, to publish those results which I have as yet obtained.

The original source of fousel oil, from which Dumas and Cahours were supplied with material for their investigations, was the alcoholic fermentation of potatoes; and hence the name potato oil, which has been given to this compound.

All the subsequent investigators appear to have worked on a similar product, with the exception of Balard, from whose paper we learn that the same substance exists in the inferior brandies prepared from wine. If, after the alcoholic liquors have passed over, the distillation of the cuticle of the grapes is continued for some time, an oily product is obtained, which, according to Balard's experiments, chiefly consists of œnanthic ether and fousel oil.

\* Ann. de Chim. et de Phys., Juillet, 1834.

† Idem, T. LXXV. p. 193.

‡ Idem, 3 sér. t. XII. p. 294

§ Erdmann's Journal, Bd. XXXI. p. 1.

|| Liebig's Annalen, Bd. LV. p. 166.

¶ Idem, Bd. LXV. 288.

\*\* Jahrbuch der Pharmacie, Bd. XIV. p. 1.

†† October, 1848.

The substance which served for the preparation of my compounds, was procured from Mr. Bowerbank, who separates it in considerable quantity during the latter stages of the distillation of common corn spirit. I mention this fact because former investigations of fousel oil derived from this source (*Getreide-fousel oil*), have not exhibited the presence of amilic alcohol. Neither Mulder\* nor Kolbe,† who examined this kind of fousel oil, mention anything about the presence of this compound; it appears that these chemists have operated upon altogether a different product. The oily liquid occurring along with cenanthic acid, cenanthic ether (Mulder), and margaric acid (Kolbe), which they describe under the name of corn oil, exhibits in its composition (Mulder) no resemblance to the fousel oil of the potato fermentation; it is probable that they examined only the very last products of the distillation, collected after the amilic alcohol had passed over.

From the experiments which I am going to describe, it is evident that the fousel oil obtained in the distillation of spirit from barley is perfectly identical with potato oil. As obtained from the distillery, the oil still contains alcohol and water, but no other impurities. On rectification, it begins to boil at  $85^{\circ}$  ( $185^{\circ}$  F.); after about one-third has passed over, the ebullition becomes constant at  $132^{\circ}$  ( $269.6^{\circ}$  F.), the boiling point of pure hydrated oxide of amyl; at this temperature the whole of the remaining liquid distils. It was evident that the product did not contain any oil of a higher boiling point.

It remained, however, to ascertain the composition of the distillate which had been collected below  $132^{\circ}$  ( $269.6^{\circ}$  F.). Chemists are acquainted with a variety of cases in which, of late, butyric and metacetonic acids have been observed as products of fermentative processes very similar to the acetic fermentation; these processes are, however, up to the present moment, by no means so well understood in their different stages as we understand the conversion of sugar into alcohol, or that of alcohol into acetic acid.

The remarkable parallelism which formic, acetic, metacetonic, butyric, and valerianic acids present in all directions, render it, to a certain extent probable, that wherever we meet with these acids as products of fermentation, their formation is preceded by that of alcohols similar to pyroxilic spirit, alcohol, and fousel oil.

It appeared by no means improbable, that the first product of the distillation might contain the alcohol of metacetonic or of butyric acid. In order to answer this question, to which my attention was

\* Liebig's Annalen, Bd. xxiv. p. 248.

† Idem, Bd. xli. p. 35.

particularly directed by Dr. Hofmann, I re-distilled the earlier distillates with particular care, removing the water by means of chloride of calcium, fractioning at intervals of five degrees, and separating the alcohol and fousel oil which came over in the beginning and at the end of the distillation. The result of repeated distillations of this kind, was the complete separation of this product into common alcohol and fousel oil, there being no other compound present.

I now proceed to the description of the compounds which I have prepared.

#### ACTION OF PHOSGENE GAS ON HYDRATED OXIDE OF AMYL.

*Carbonate of oxide of amyl.*—Chloro-carbonic ether obtained by Dumas\* in the reaction of chloro-carbonic acid (phosgene gas) on absolute alcohol, and urethane (carbamate of ethyl), produced by the subsequent treatment of the new ether with ammonia, are not yet represented in the amyl series. To the preparation of these my attention was first directed.

Fousel oil absorbs phosgene gas with great avidity, heat being evolved during the process; one gramme of fousel oil absorbed about one liter of gas.

When perfectly saturated, hydrochloric acid was abundantly evolved, the liquid assuming a rich amber colour and separating into two strata, the lower one consisting of a very small quantity of accidental water, strongly charged with hydrochloric acid.

The new compound floating on the surface was now mixed with nearly an equal volume of distilled water, which, after having been in contact with it for a quarter of an hour, was removed by means of a pipette. The water, although strongly impregnated with hydrochloric acid, had by no means removed the last traces of the gas; the compound was therefore left for some time in contact with protoxide of lead, and finally dried by means of chloride of calcium. On submitting the liquid to distillation, with the view of determining its boiling point, it became at once evident that it could not be heated without suffering decomposition; it blackened immediately, torrents of hydrochloric and carbonic acids being evolved, and the boiling point rapidly rising from  $150^{\circ}$  ( $302^{\circ}$  F.) to  $224^{\circ}$  ( $435.2^{\circ}$  F.), where it became perfectly stationary. To obtain the key to this peculiar decomposition, it was necessary to study the oily product which distilled during the evolution of carbonic and hydrochloric acids. This product, after another rectification, became a perfectly clear and transparent liquid, of an agreeable odour, very

\* Ann. de Chim et de Phys. t. LIV. p. 225.

different from the original odour of fousel oil that had been treated with phosgene gas; it had a specific gravity of 0.9144 at 15.5° (60° F.), and its constant boiling point at 224° (435.2° F.), indicated a definite compound.

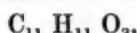
By combustion with protoxide of copper, the following results were obtained.

I.	0.2480	grm. of substance gave	
	0.5925	„ of carbonic acid and	
	0.2458	„ of water.	
II.	0.2158	„ of substance gave	
	0.5165	„ of carbonic acid and	
	0.2110	„ of water.	

Per centage composition :

	I.	II.
Carbon . . . .	65.15	65.23
Hydrogen . . . .	11.01	10.87

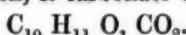
The simplest atomic expression for these numbers is the formula :



as may be seen from the following comparison of the theoretical values with the experimental results :

	Theory.	Mean of the experiments.	
11 equivs. of carbon . . .	66	65.15	65.19
11 „ of hydrogen . .	11	10.89	10.94
3 „ of oxygen . .	24	23.77	—
<hr/>		101	100.00

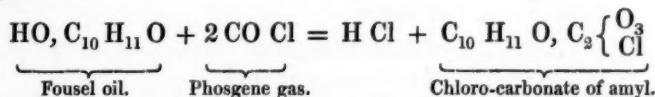
The new compound, then, is carbonate of oxide of amyl :\*



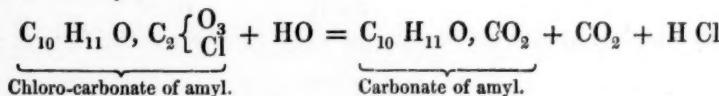
If the analysis had left a doubt regarding its nature, this would

\* The production of the carbonate of oxide of amyl, by means of phosgene gas, as described by Mr. Medlock, seemed to point out an easy method of obtaining the carbonates of the ethers in general. Chemists know the remarkable, but still somewhat mysterious process, by means of which the carbonate of ethyl was first obtained by Dr. Ettling, viz., by the action of potassium on oxalic ether (Liebig's Annalen, v. xix. p. 17). The corresponding methyl compound has never been prepared. In order to see whether chloro-carbonate of methyl and of ethyl undergo a similar decomposition, I induced Mr. Charles Bloxam to study the action of water on these compounds. From these experiments it is evident this chloro-carbonate of ethyl is likewise acted upon by water, but too slowly to give a satisfactory method of preparing the carbonate. After four or five distillations with water, only a very small quantity of the chloro-carbonate is decomposed. The presence of bases destroys the compound altogether. It remains to be tried whether a different result might not be obtained by the action of water at a higher temperature under pressure.—DR. A. W. HOFMANN.

have been dispelled by its behaviour with the alkalies. When treated with an alcoholic solution of potash, the suffocating odour of fousel oil became at once perceptible, while the liquid solidified into a crystalline mass of carbonate of potash. The formation of carbonate of oxide of amyl admits of an easy explanation. The action of phosgene gas on fousel oil is perfectly analogous to that which it exerts on alcohol, hydrochloric acid and chlorocarbonate of amyl being formed.



The chloro-carbonate of amyl, however, is a compound of very unstable character; when brought into contact with water, it is decomposed into hydrochloric acid, carbonic acid, and carbonate of oxide of amyl.



The conversion of the chloro-carbonate into carbonate had evidently taken place chiefly during the washing of the compound with water. In a second operation, therefore, the washing was altogether omitted; nevertheless, on distilling the compound after removal of the hydrochloric acid by protoxide of lead, the same phenomena as before were observed. It was quite obvious that the accidental moisture,\* which cannot be well avoided, and the water formed in the conversion of protoxide of lead into proto-chloride, must have been sufficient to effect the decomposition. It is nevertheless probable, if not certain, that the chloro-carbonate exists, and may be obtained by a very careful exclusion of every trace of moisture. The powerful odour of fousel oil saturated with phosgene gas, having nothing in common with the suffocating odour of the latter, but closely resembling that of chloro-carbonic ether, appears in favour of this opinion, which is rendered still more probable by the behaviour of this crude product

\* Both the chlorine and carbonic oxide employed for the preparation of phosgene gas had been carefully dried by sulphuric acid; the bottles, with ground-glass stoppers, in which the gases were allowed to combine, were perfectly dry; the fousel oil, likewise, was absolutely anhydrous; nevertheless the oil, when nearly saturated with gas, separated always into two strata, of which the lower one was an aqueous solution of hydrochloric acid. It is evident that on pouring the fousel oil from one bottle of phosgene gas into another, a certain amount of moisture was attracted from the atmosphere, a quantity which must have been considerable, if we reflect that this operation had to be repeated from twenty-five to thirty times.

with ammonia. It is well known that the action of ammonia on chloro-carbonate of ethyl gives rise to the formation of the substance which Dumas, the discoverer, called urethane, and which we are now in the habit of considering as the ether of carbamic acid. If the crude product of the action of phosgene gas on fousel oil is treated with an alcoholic solution of ammonia, a white precipitate is formed, which consists of two substances, chloride of ammonium and a fatty crystalline organic compound, very similar in appearance to spermaceti. By washing with water, the former was dissolved, and the latter remained in a state of purity. Unfortunately, although working with considerable quantities, I did not obtain enough of this compound for combustion; but its comportment, as well as analogy, allows the conclusion, that it was the urethane of the amyl series, produced by the action of ammonia on the small quantity of undecomposed chloro-carbonate of amyl which the mixture might have still contained at that period. There is one objection which could be made to this supposition, viz., that we know from some experiments, which have been lately published by M. Cahours,\* that carbonate of ethyl, when treated with ammonia, yields likewise urethane. In our case, however, the carbonate could not have caused the formation of this compound. I have vainly tried to obtain it by digesting for weeks pure carbonate of amyl, with an aqueous as well as an alcoholic solution of ammonia, both of which have no action upon it whatever. The existence, however, of a chloro-carbonate of amyl is by no means established by the foregoing experiments. I intend to return to this question as soon as the weather will allow a rapid preparation of phosgene gas.

*Sulphocyanide of Amyl.*—The interest naturally attached to the sulphocyanides of methyl and ethyl, has of late been considerably increased by their conversion into hyposulphomethylic and hypo-sulphethylic acids by Dr. Muspratt.

The preparation of sulphocyanide of amyl is perfectly analogous to that of the corresponding ethyl and methyl compounds.

Two parts of sulphamylate of lime, intimately mixed with one part of finely-powdered sulphocyanide of potassium, were introduced into a retort capable of holding twice the amount of the mixture; on the application of heat, some water and fousel oil distilled over, possessing a very peculiar odour; on increasing the temperature, a considerable quantity of a reddish-yellow oil passed over, having the same remark-

\* Compt. rend. T. xxi. p. 629.

able odour. This oil is the sulphocyanide of amyl.\* The crude product was washed with distilled water, and subsequently digested with chloride of calcium, in order to remove the last trace of moisture, which it retains with great pertinacity. The anhydrous oil possesses the property of dissolving chloride of calcium in considerable quantity, from which it has to be separated by distillation.

The anhydrous compound, when submitted to distillation, commenced boiling at  $150^{\circ}$  ( $302^{\circ}$  F.), the thermometer continuing to rise to  $195^{\circ}$  ( $383^{\circ}$  F.), at which point it became almost stationary, by far the greater part of the product distilling over at about this temperature. The latter portion, when re-distilled, boiled at the constant temperature of  $197^{\circ}$  ( $386.6^{\circ}$  F.). The following analyses were made of the product collected at this temperature.

I. 0.2816 grm. of sulphocyanide, burned in a tube containing oxide of copper, oxide of lead, and copper turnings, gave :  
0.5748 grm. carbonic acid, and  
0.2280 " water.

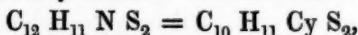
II. 0.2894 " of sulphocyanide gave :  
0.5914 " carbonic acid, and  
0.2320 " water.

III. 0.3195 " of sulphocyanide, burned with soda-lime, gave :  
0.5525 " of the double salt of platinum and ammonium.

Per centage composition :

	I.	II.	III.
Carbon . . . . .	55.66	55.73	—
Hydrogen . . . . .	8.99	8.90	—
Nitrogen . . . . .	—	—	10.84

These numbers closely coincide with the formula :



as may be seen by the following table :

	Theory.	Mean of experiments.	
12 eqs. of Carbon . . . . .	72	55.81	55.69
11 " Hydrogen . . . . .	11	8.52	8.95
1 " Nitrogen . . . . .	14	10.85	10.84
2 " Sulphur . . . . .	32	24.82	—
1 eq. of sulphocyanide of amyl . . . . .	129	100.00	

\* To avoid violent intumescence, the sulphamylate of lime and sulphocyanide of potassium should be dried as perfectly as possible.

This compound, when perfectly pure, has an oily appearance, and a slightly yellow colour, which becomes darker by keeping. It is miscible with alcohol and ether in all proportions, but separates again on the addition of water, in which it is nearly insoluble. Its boiling point is exactly  $197^{\circ}$  ( $386\cdot6^{\circ}$  F.), which nearly corresponds with the temperature calculated from the boiling point of sulphocyanide of ethyl, as observed by Cahours.\*

$$146^{\circ} + 3 \times 19 = 203^{\circ}.$$

At  $15.5^{\circ}$  ( $60^{\circ}$  F.), the specific gravity of the sulphocyanide of amyl is 9381.1.†

#### ACTION OF NITRIC ACID ON SULPHOCYANIDE OF AMYL.

*Hyposulphamylic acid.*—Nearly equal parts of sulphocyanide of amyl and moderately strong nitric acid were introduced into a small retort, and distilled at a gentle temperature after the very violent action had ceased. In order to complete the re-action, nitric acid must be occasionally added, and the distillate returned to the retort, until the whole of the sulphocyanide has disappeared. In this process, carbonic acid, nitrogen, binoxide of nitrogen, and nitrous acid, are abundantly evolved; sulphuric acid likewise is formed by the oxidation of a portion of the sulphur; the quantity, however, of this acid greatly varies with the strength of the nitric acid employed; if moderately dilute, scarcely a trace of it is produced, but on the contrary, if fuming acid be employed, a dense precipitate of sulphate of baryta is obtained by the addition of chloride of barium; as soon as the action had entirely ceased, the liquid was evaporated on a water-bath until the nitric acid was expelled; a reddish oily fluid remained, possessing a pungent alliaceous odour and a hot acrid taste. It was then treated with water, in which it readily dissolved, filtered, and again evaporated. The liquid was thus freed from the last traces of nitric acid, and rendered almost colourless. In order to obtain the acid in a state of perfect purity, I prepared the lead-salt by saturating an aqueous solution with the carbonate of that metal. After treating the solution with hydrosulphuric acid, filtering, and careful evaporation on a water-bath, until the last traces of hydrosulphuric acid were expelled, the pure acid remained as a colourless oily liquid, which, when exposed in vacuo over sulphuric

\* Ann. de Chim. et de Phys. 3 sér. T. xviii. p. 257.

† Sulphocyanide of amyl, although in an impure state, has been likewise obtained by M. O. Henry, who analysed a product boiling between  $195^{\circ}$  ( $383^{\circ}$  F.) and  $211\cdot1^{\circ}$  ( $412^{\circ}$  F.), which yielded, on combustion, one per cent of carbon above the theoretical proportion.—*Journal de Pharmacie*, Oct. 1848.

acid, gradually became a granular crystalline mass, attracting moisture, and liquefying immediately on exposure to the air.

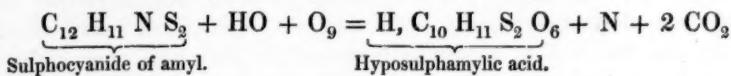
Hyposulphamylic acid, for this is the compound in question, cannot be heated without suffering decomposition ; it evolves a very disagreeable odour, a charred mass remaining behind.

The formula for hyposulphamylic acid, as resulting from the analysis of its salts, is :



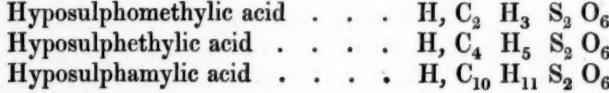
It accounts easily for the formation of this compound, the sulpho-cyanogen being decomposed under the influence of nitric acid; the sulphur is oxidized and the cyanogen evolved in the form of nitrogen and carbonic acid.

The following equation represents this decomposition:



55 3.3 11 6.3 3 3 3

Hyposulphamyllic acid corresponds to hyposulphethylic and hyposulphomethylic acids lately obtained by Dr. Muspratt\* by analogous reactions, the latter having been previously obtained by Dr. Kolbe† as a product of the metamorphosis of chloro-carbo-hypsulphuric acid, when under the influence of galvanic electricity.



I have examined the compounds of hyposulphamylic acid with barytes, with protoxide of copper and protoxide of lead.

*Hyposulphamylate of Barytes*.—This salt is obtained by saturating an aqueous solution of the acid with carbonate of barytes; when perfectly neutralized, the filtered liquid is slowly evaporated on a water-bath, and allowed to crystallize. This salt is extremely soluble, both in water and alcohol, and can be obtained in well-formed crystals only by allowing the aqueous solution to evaporate spontaneously, when brilliant pearly scales are deposited.

I. 0.4880 grm. of the salt, dried at  $100^{\circ}$  ( $212^{\circ}$  F.), gave:

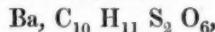
0.4915 „ carbonic acid = 27.46 per cent. of carbon,  
 0.2295 „ water = 5.22 „ of hydrogen.

II. 0.3015 " of the salt gave 0.1594 sulphate of barytes = .1170  
grm. barium.

\* Quarterly Journal of the Chemical Society, vol. 1. p. 45.

<sup>†</sup> Memoirs of the Chemical Society, vol. II. p. 360.

These numbers lead to the formula :



as may be seen from the following table :

	Theory.	Experiment.
10 eqs. of Carbon . . . . .	60	27.31
11 " " Hydrogen . . . . .	11	5.00
2 " " Sulphur . . . . .	32	14.56
6 " " Oxygen . . . . .	48	21.88
1 " " Barium . . . . .	68.64	31.25
1 eq. of Hyposulphamylate of Barytes	219.64	100.00

I have determined the amount of water lost at 100° (212° F.); it is much less than one equivalent, showing that the salt is anhydrous.\*

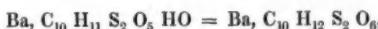
*Hyposulphamylate of Copper.*—It is difficult to obtain this salt in well-defined crystals; the best method, however, of preparing it, is to saturate an aqueous solution of the acid with carbonate of copper, to evaporate the filtered solution on a water-bath, to dryness, and to treat the residue with absolute alcohol. The filtered solution deposits minute crystalline plates, when allowed to evaporate spontaneously in narrow tubes.

I. 0.4960 grm. of the dried salt, burned with chromate of lead, gave :  
 0.5936 " carbonic acid = 32.63 per cent. carbon,  
 0.2754 " water = 6.16 per cent. hydrogen.  
 0.3970 " of the dried salt gave : 0.863 grm. oxide of copper  
 = 17.33 per cent. copper.

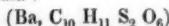
These numbers lead to the formula :



\* The acid prepared by Mr. Medlock is evidently identical with the compound which Messrs. Gerathewohl and Erdmann<sup>(1)</sup> obtained as a product of the decomposition of the mercaptan of the amyl series by means of nitric acid, although these chemists adopt a different formula for that compound. The formula which they give for the barytes-salt of their acid is :



differing from Mr. Medlock's formula :



by one equivalent of hydrogen. In four hydrogen determinations, however, a deficiency was found, oscillating between 0.2 and 0.4 per cent., whilst our analyses generally give a slight excess. A similar objection can be made to the analysis of several salts of the acid, obtained by the action of nitric acid on the mercaptan of the ethyl series. It would be interesting to repeat the analysis of the barytes-salt, on which the formula



assigned to this acid, is principally founded. It is very probable that the opinion of M. Gerhardt respecting it will prove correct.—Dr. A. W. HOFMANN.

(1) Erdmann's Journal, vol. XXXIV. p. 447.

as the following comparison will show :

	Theory.	Experiment.
10 eqs. of Carbon . . . . .	60	32.84
11 " " Hydrogen . . . . .	11	6.02
2 " " Sulphur . . . . .	32	17.52
6 " " Oxygen . . . . .	48	26.29
1 " " Copper . . . . .	31.66	17.33
1 " " Hyposulphamylate of Copper	182.66	100.00

The salt does not contain any water of crystallization.

*Hyposulphamylate of Lead.*—This salt is prepared in the same manner as the preceding ; it is extremely soluble in water, and may be obtained in beautiful satiny needles by allowing an aqueous solution to evaporate spontaneously. When heated, it is decomposed, evolving a most disagreeable odour, sulphide of lead remaining.

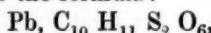
I. 0.5690 grm. of the salt, dried at 100° (212° F.), and burned with chromate of lead, gave :

0.4936 " carbonic acid = 23.65 per cent. carbon,  
0.2168 " water = 4.23 " hydrogen.

II. 0.3340 " of the dried substance gave :

0.1986 " sulphate of lead = 40.63 per cent. lead.

These numbers lead to the formula :



as may be seen by the following table :

	Theory.	Experiment.
10 eqs. of Carbon . . . . .	60	23.57
11 " " Hydrogen . . . . .	11	4.32
2 " " Sulphur . . . . .	32	12.57
6 " " Oxygen . . . . .	48	18.85
1 " " Lead . . . . .	103.56	40.68
1 " " Hyposulphamylate of Lead . .	254.56	100.00

This salt is likewise anhydrous.

The following table includes the salts of hyposulphamylic acid, which I have analysed :

Barytes salt . . .	Ba, C <sub>10</sub> H <sub>11</sub> S <sub>2</sub> O <sub>6</sub>
Copper " . . .	Cu, C <sub>10</sub> H <sub>11</sub> S <sub>2</sub> O <sub>6</sub>
Lead " . . .	Pb, C <sub>10</sub> H <sub>11</sub> S <sub>2</sub> O <sub>6</sub>

I have prepared various other compounds of the amyl series, but their analyses not being yet complete, I refrain from entering into details. I may, however, mention that I have studied the action of

potassium on cyanide of amyl, and that of chloride of zinc on fousel oil. In the former process, simultaneously with a gaseous product, a beautiful organic alkaloid, corresponding to kyanethine, is formed. In the latter I have obtained the liquid hydrocarbons of M. Balard, accompanied by a gaseous carbo-hydrogen, of the same composition as olefiant gas, the production of which has not been observed before. The description of these compounds I shall shortly communicate to the society.

I cannot conclude without expressing the great obligation I am under to Professor Hofmann for his valuable aid and unremitting attention during the prosecution of my experiments.

## NOTICES

OF

### PAPERS CONTAINED IN THE FOREIGN JOURNALS.

*Researches on the hydrates.\**—Some chemists have compared the hydrated acids to hydracids, in which the hydrogen is combined with a compound radical; others have attributed the acid properties of the hydrated acids to the proportion of water which they contain; and again, others have compared certain hydrated acids to the oxygen compounds, in which a part of the oxygen has been replaced by an equivalent quantity of hydrogen, &c., &c. M. Fremy, having studied the functions of water in the acids, oxides and salts, has arrived at the following conclusions:

In most, cases, it is not the water, which determines the acidity of the acids; as a large number of acids may be rendered anhydrous without losing their property of combining with bases, and of expelling from their saline combinations those acids which are of a less fixed character.

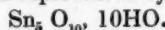
Several hydrates, as those of the protoxide of tin, deutoxide of copper, ( $\text{CuO}$ ), sesquioxide of chromium, which may be viewed as weak acids, are indebted for their acidity to the water which they contain, and become insoluble in the alkalies on losing their water of combination. It is impossible to isolate the combinations of these hydrates with water, because the water which determines the acidity of the hydrate is evolved during the evaporation of the salt, and the oxide is then precipitated in the anhydrous state.

The second compound of tin with oxygen presents a curious example of one oxide forming two acids differing not only in their properties, but also in their atomic weight.

One of these acids, stannic acid, is represented by the formula :



the stannates are represented by  $\text{Sn O}_2 \cdot \text{MO}$ . The other acid, the metastannic acid, has a composition represented by



This acid, dried in vacuo, is converted into  $\text{Sn}_5 \text{O}_{10} \cdot 5\text{HO}$ , and by desiccation at a temperature of  $130^\circ \text{C}$ . ( $266^\circ \text{F}$ .) into  $\text{Sn}_5 \text{O}_{10} \cdot 4\text{HO}$ .

The neutral metastannates of potash and soda are represented by  $\text{Sn}_5 \text{O}_{10} \cdot \text{Ka O} \cdot 4\text{HO}$  and  $\text{Sn}_5 \text{O}_{10} \cdot \text{Na O} \cdot 4\text{HO}$ . When a metastannate is

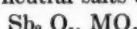
\* Ann. de Chim. et de Phys. xxiii. 385.

entirely deprived of water, the metastannic acid loses its acid properties and separates from the base with which it was in combination.

Metastannic acid, therefore, not only possesses a different equivalent to stannic acid, but also differs in the property of forming salts with bases which cannot exist without water.

Metastannic acid must consequently be classed with those acids which owe their acidity to their water of hydration.

The second grade of combination of antimony with oxygen is also capable of forming two distinct acids; the one is antimonic acid, which, in union with bases, produces neutral salts of the formula:



The other is an acid which the author calls meta-antimonic acid, and is capable of forming two classes of salts with bases. These are represented by the formulæ:



The meta-antimonates are characterized by the property of precipitating the salts of soda from solution, which is not observed in the antimoniates. The antimoniates may be transformed into meta-antimonates by the agency of an excess of alkali.

Water exerts considerable influence upon the properties of the antimoniates and meta-antimonates; these salts are soluble or insoluble, according to the proportion of water which they contain.

Water likewise appears to have an influence upon the basic properties of certain metallic oxides; thus the hydrated protoxide of copper dissolves in all acids forming salts of the protoxide of copper, while anhydrous protoxide of copper has entirely lost the property of combining directly with acids, being converted by the latter into metallic copper, and the deutoxide of the metal.

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*On the estimation of nitrogen.\**—Nöllner recommends the following process for the estimation of nitrogen, particularly when a speedy result is desirable, as in cases of commercial analysis, in determining the relative values of manures, &c. The substance under examination is heated in a tube with a mixture of caustic lime, as in Will and Varentrapp's process, and the ammonia that is evolved is conducted by a tube into a light bottle containing a solution of pure tartaric acid in absolute alcohol. The tube conveying the ammonia is not allowed to dip into the liquid of the first bottle, but the bottle is furnished with a safety tube, and likewise with another second tube, leading through the cork of the first into the same solution in a second bottle, which in like manner is connected with a third bottle. The whole of the ammonia is thus collected and precipitated in the form of bitartrate of ammonia, a salt which is perfectly insoluble in strong alcohol, with which liquid it may therefore be washed upon a weighed filter, and when dried at a temperature of 80° C. (176° F.), yields the

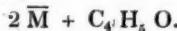
\* Ann. der Chem. und Pharm. LXVI. 314.

amount of ammonia in the original substance; 100 parts of the salt thus dried containing 10.2 per cent. of ammonia = 8.4 per cent. of nitrogen. The author has confirmed the accuracy of the process by a series of experiments, chiefly conducted with crude materials used in the manufacture of yellow prussiate of potash.

*On mellitic acid.\**—The composition of mellitic acid was first ascertained by Liebig and Wöhler, who assigned it the formula,  $C_4 O_3$ .

Pelouze and Liebig, at a later period, represented the acid by the formula  $C_4 O_4 H$ . Messrs. Erdmann and Marchand have investigated the subject, with the view of determining which of these formulae is correct. In preparing the acid and the insoluble salts in the usual manner, by precipitating the mellitate of ammonia with salts of lead, copper, silver, &c., they found that an acid mellitate of ammonia accompanied the metallic salts, and clung to the acid when the latter were decomposed with sulphuretted hydrogen. They prefer, therefore, to prepare the acid by boiling the salt of ammonia with an excess of barytes, digesting the barytes compound with sulphuric acid, and crystallizing repeatedly from water, to remove the sulphuric acid. The insoluble salts were obtained by precipitating neutral salts of the bases with the pure acid.

The analysis of the silver-salt, which is anhydrous, gave the formula  $C_4 O_3$  for the acid, which, therefore corroborates the original statements respecting its constitution. A series of salts have been prepared and analyzed by the authors, and likewise a conjugate acid, with ether, analogous to the sulphovinic acid, having the composition expressed by the formula :

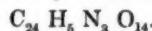


*On mellitic acid and its products of decomposition.†*—Schwartz has investigated several salts of mellitic acid and likewise the composition of the pure acid; his results coincide with those of Erdmann and Marchand, the formula for the crystallized acid being  $C_4 O_3$ ,  $HO$ . The author did not succeed in obtaining combinations of this acid with the oxides of ethyl or methyl; his experiments corroborate those of Wöhler upon the conversion of mellitate of ammonia at a high temperature into euchronic acid and paramide, but a much larger proportion of the former substance, and consequently less of the latter, is obtained when the heated mellitate of ammonia is digested repeatedly with water, at a temperature of from  $40^{\circ}$  to  $50^{\circ}$  ( $104^{\circ}$  to  $122^{\circ}$  F.). It appears, therefore, that the residue, after the first action of water, contains either an acid euchronate of ammonia, which is only dissolved by the prolonged action of warm water, or that the paramide, when it has not been too strongly heated during its production, possesses the property, in contact with water at that temperature, of being converted into euchronate

\* Journ. für prakt. Chem. XLIII. 129.

† Ann. der Chem. und Pharm. LXVI. 47.

of ammonia. When paramide is digested in caustic ammonia, it assumes a yellow colour, becomes very voluminous, and partially dissolves; if this solution is allowed to fall immediately into hydrochloric acid, a snow-white pulverulent body is deposited, which, viewed under the microscope, presents a mass of very fine needles. This body is somewhat soluble in hot water, and is again deposited in the form of a powder when the solution cools. With zinc the blue reaction of euchronic acid is observed. Ammonia dissolves the substance, which is again precipitated by hydrochloric acid. If the solution is heated, or allowed to remain at rest for a day, mellitate of ammonia alone can be detected in it. Dried in *vacuo*, and heated to 170° C. (338° F.), this substance lost from 2.820 to 3.286 per cent. of water. The analyses of the dry substance yielded the formula :



The author proposes to call this body *paramidic acid*, and its formation may be explained upon the assumption that 3 equivs. of paramide have combined with 2 equivs. of water, or that 2 equivs. of euchronic acid have been united with 1 equiv. of ammonia and 2 equivs. of water.

*Note on sulphurous acid and on its combination with water.*\*—It was observed about twenty years ago by M. de la Rive, that moist sulphurous acid, when surrounded by a freezing mixture, deposited thin, white, crystalline leaflets, which resembled the crystals of the hydrate of chlorine, and which were found to contain about 20 of sulphuric acid to 80 of water. The ice obtained by M. Boutigny by the evaporation of sulphuric acid in contact with water, is also more or less impregnated with sulphurous acid, and is not pure crystallized water. M. Pierre has repeated the experiments of de la Rive, preparing the substance under different circumstances. In one case, aqueous vapour was allowed to flow in small quantity into a vessel cooled to 6° or 8° C. (43°—47° F.) simultaneously with a large excess of gaseous sulphurous acid. In another, the author exposed a very concentrated solution of sulphurous acid in water to a temperature approaching 0° C. (32° F.) for some time, when crystals resembling nitrate of potash were deposited. The analysis of the compound thus produced was effected by immersing the crystals in an aqueous solution of chlorine, which converts the sulphurous into sulphuric acid, and generates hydrochloric acid at the same time. The author likewise endeavoured to ascertain whether the whole of the water in this compound was contained as basic water, or whether one portion played the part of basic water, while another portion was in combination as water of crystallization. He endeavoured, with this object in view, to produce some other hydrates of the acid. The following are the results of his experiments :

Sulphurous acid, in combining with water, yields a crystalline hydrate,

\* Ann. de Chem. et de Phy. xxiii, 416.

containing rather more than 28 per cent of acid, and which may be represented by the formula :



This hydrate crystallizes with great ease in a concentrated solution of sulphurous acid at a temperature of  $2^{\circ}$  or  $3^{\circ}$  C. ( $36^{\circ}$ — $38^{\circ}$  F.) above the temperature of melting ice.

At a temperature of  $-10^{\circ}$  or  $-12^{\circ}$  C. ( $14^{\circ}$  to  $12^{\circ}$  F.) anhydrous sulphurous acid does not dissolve water in appreciable quantity under the ordinary pressure.

At a temperature 10 or 12 degrees above zero C. ( $50^{\circ}$ — $54^{\circ}$  F.), and under a pressure of several atmospheres, sulphurous acid may be frequently shaken for a length of time with water without absorbing a notable quantity of the latter; the proportion of water which it then retains is below  $0.005$ , and must probably be considered as mechanically mixed with it.

*On the nitrites.\**—The nitrites are a series of salts that have been but little investigated; they are produced by the action of heat upon the nitrates. Several of these salts have been investigated by N. W. Fisher. The salts of soda, potash, barytes, and strontian are obtained by heating the respective nitrates to redness, dissolving in water, and allowing the excess of nitrate to crystallize; (the nitrates of potash and soda afford a little caustic alkali when heated to redness, which is neutralized with acetic acid); alcohol is then added to the solution, which precipitates, after a time, the remainder of the nitrate, and the nitrite remaining in solution may be crystallized over sulphuric acid, the greater portion of the alcohol having been removed. The salts of lime, ammonia, and magnesia were obtained from the chlorides by nitrite of silver, which was itself prepared from the nitrate by means of nitrite of potash; the metals, zinc, cadmium, lead, copper and cobalt, reduce the nitrite of silver, and the oxides enter into combination with nitrous acid. Tin, bismuth, mercury and antimony, although they reduce the silver from the nitrite, do not combine with the acid, and iron and nickel do not even reduce the salt of silver.

The salts of the alkalies and earths are mostly deliquescent, while those of the heavy metallic oxides are persistent in the air; several of the latter form double salts with nitrite of potash; amongst these, the double salts of silver, palladium, lead, nickel, and cobalt, have been prepared and described by the author.

*On the phosphates.\**—In the Memoirs of the Chemical Society, vol III. p. 273, some researches by Maddrell are detailed, upon the modification of metaphosphoric acid contained in the insoluble metaphosphate of soda. This salt is produced simultaneously with a soluble metaphosphate, by the

\* Pogg. Ann. LXXIV. 115.

† Ann. der Chem. und Pharm. LXV. 304.

action of a temperature below the fusing point, upon microcosmic salt. The salts examined by Maddrell were all insoluble and anhydrous, and answered to the formula  $MO_3 PO_6$ . They may be obtained by mixing solutions of the metallic oxides with dilute phosphoric acid, evaporating the solution, and heating the residue to a temperature of  $600^{\circ} F.$  Messrs. Fleitmann and Henneberg have investigated the salts of that modification of metaphosphoric acid which remains in solution, combined with soda, after the deposition of the above insoluble soda-salt. The most profitable method of obtaining a large proportion of the soluble metaphosphate, is by removing the heated mass from the fire while it still exhibits a powerful acid reaction, reducing it to powder, and again exposing it to heat, without allowing it to cake together. The operation is stopped when the mass still exhibits a slight acid reaction; it is then extracted with cold water, and the solution allowed to deposit crystals by spontaneous evaporation. The fused metaphosphate of soda may be converted into the crystalline salt by a very slow process of cooling. The crystalline product dissolves in warm water, and the solution separates into two strata, the more abundant of which contains the crystalline salt. The other salts of this acid were obtained by double decomposition with the salts of the metallic oxides. The following metaphosphates have been prepared and analyzed by the authors:

Metaphosphate of soda . . . .	$3(NaO, PO_3) + \frac{1}{2} HO + 11\frac{1}{2} Ag.$
Metaphosphate of silver . . . .	$3(AgO, PO_3) + 2 HO.$
Metaphosphate of lead . . . .	$PbO, PO_3 + HO.$
Metaphosphate of barytes . . . .	$3(BaO, PO_3) + 6 HO$ (loses 2 HO at $212^{\circ} F.$ )
Metaphosphate of soda and barytes . . . .	$\left. \begin{array}{l} (2BaO, NaO), 3 PO_3 + 8 HO \\ \text{loses } 5HO \end{array} \right\} 212^{\circ} F.$

None of these salts could be obtained anhydrous at  $212^{\circ}$ , but the latter mode of preparing the soda-salt proves that this water is not essential to their constitution.

The authors consider that the relations in which these salts combine with water are incompatible with the assumption of a monobasic metaphosphoric acid in them, and prefer to represent the different modifications of the metaphosphoric acid as of a polymeric character.

Thus the salts of the vitreous acid would be represented by  $MO, PO_3$ ; those of the insoluble acid described by Maddrell, by  $2 MO, 2 PO_3$ ; and the preceding crystalline salts by  $3 MO, 3 PO_3$ .

The ordinary assumption, in which most authors have adopted Graham's views, that the acid in the common phosphate, in the pyrophosphates and metaphosphates, is one and the same acid, which is capable of saturating different proportions of base, appearing inconsistent with acknowledged theory, Messrs. Fleitmann and Henneberg, starting from a constant proportion, (6 equivs.), of base as the fixed point, propose to consider the salts of phosphoric acid as combinations of a polymeric acid,  $P_2 O_{10}, P_3 O_{15}, P_4 O_{20}$ ,

&c., the missing members of which series they have been enabled to fill up. The series of phosphates would thus assume the following form :

Common phosphate . . . . .	6 MO + 2 PO <sub>5</sub> .
Pyrophosphate . . . . .	6 MO + 3 PO <sub>5</sub> .
New phosphate of Fleitmann and Henneberg .	6 MO + 4 PO <sub>5</sub> .
" " "	6 MO + 5 PO <sub>5</sub> .
Metaphosphate . . . . .	6 MO + 6 PO <sub>5</sub> .

The phosphate of the form 6 MO + 4 PO<sub>5</sub> was obtained by fusing 76·86 parts of vitreous metaphosphate of soda with 100 parts of anhydrous pyrophosphate of soda, or by the fusion of 187·27 parts of metaphosphate of soda with 100 parts of the compound 3 NaO, PO<sub>5</sub>. The substances were ground together in a mortar, and kept in a state of fusion for some time, during which the mass was stirred. The fused product is pulverized and a quantity of warm water poured over it, insufficient to dissolve it completely, and after digesting for some time, the residue is separated by filtration. The solution is allowed to crystallize over sulphuric acid, or exposed to the air. The crystals are often not deposited before twelve or twenty-four hours, and the whole liquid then frequently solidifies to a granular mass, consisting, when viewed under the magnifier, of delicate thin laminæ. These are thrown upon a funnel, and when washed with a little cold water from the thick liquid, may be pressed between bibulous paper, and are then quite pure. The salt is liable to be decomposed by a high temperature, and even under ordinary circumstances, into the two compounds 2 NaO HO, PO<sub>5</sub> and NaO 2 HO, PO<sub>5</sub>, the former of which being less soluble than the latter, not unfrequently accompanies the above salt in small quantity.

The salt represented by the formula 6 NaO, 4 PO<sub>5</sub>; is soluble in about 2 parts of cold water, and has at first a slight alkaline reaction, which, however, soon passes into the opposite, or becomes acid from the formation of the latter of the above products of its decomposition.

The mixture which yielded the salt 6 NaO, 4 PO<sub>5</sub> by fusion, when dissolved in water and allowed to crystallize, deposited unchanged pyrophosphate of soda, proving that the fused salt is not simply a mixture of the two constituents from which it has been produced.

The corresponding salts of silver, magnesia, barytes, and lime of this form, were obtained by double decomposition and also exhibited properties different from those of mixtures of pyrophosphate and metaphosphate.

Berzelius mentions two salts of phosphoric acid, which he terms sesqui-phosphates, and which correspond, when fused, completely with these compounds.

The one, a silver-salt, he represented by the formula 3 Ag O, 2 PO<sub>5</sub>. The other, is a salt of barytes of similar constitution.

The reactions of this acid accord it a place intermediate between meta- and pyrophosphoric acids.

The other member of the series, 6 NaO, 5 PO<sub>5</sub>, was obtained in a pre-

cisely similar manner, 100 parts of pyrophosphate of soda being fused with 307·5 parts of metaphosphate of soda. The compound crystallizes with greater difficulty than the preceding. It presents a glassy appearance after fusion, bearing the greatest resemblance to metaphosphate of soda. The silver-salt of this form only was analysed.

*On some isomorphous double salts of chloride of ammonium with chlorides of the magnesian class.\**—Hautz has ascertained the existence of two series of salts, containing 2 equivs. of a metallic chloride in combination with 1 equiv. of chloride of ammonium, and which only differ in their respective amounts of water. Of these the following :

Chloride of magnesium and ammonium  $\text{NH}_4\text{Cl}$ , 2  $\text{MgCl}$ , 12 HO,

Chloride of nickel and ammonium  $\text{NH}_4\text{Cl}$ , 2  $\text{NiCl}$ , 12 HO, and

Chloride of copper and ammonium  $\text{NH}_4\text{Cl}$ , 2  $\text{CoCl}$ , 12 HO,

all crystallize with 12 atoms of water, but the cobalt-salt has a different crystalline form from the magnesium and nickel-salts, and corresponds to the following salts which crystallize with only 4 atoms of water, 3 of which they lose at a temperature of 100°.

Chloride of manganese and ammonium  $\text{NH}_4\text{Cl}$ , 2  $\text{MnCl}$ , 4 HO,

Chloride of zinc and ammonium  $\text{NH}_4\text{Cl}$ , 2  $\text{ZnCl}$ , 4 HO,

Chloride of copper and ammonium  $\text{NH}_4\text{Cl}$ , 2  $\text{CuCl}$ , 4 HO.

A salt of zinc, of the following composition, was likewise obtained :



*On the separation of the alkalies from magnesia by means of carbonate of silver.†*—Sonnenschein recommends the use of oxide of silver in quantitative analysis, on account of its powerful basic properties, and the ease with which it is removed from solution. The carbonate being more easy of purification, is preferred to the pure oxide for this purpose. The chlorides of the bases to be separated are evaporated to dryness, which operation removes any ammoniacal salts that might be present, and a portion of the acid from the magnesia. The dry mass is drenched with water, and then boiled with carbonate of silver until the liquid exhibits a distinctly alkaline reaction. It is recommended to boil the solution for at least ten minutes, under constant agitation ; the solution is filtered while hot, and the precipitate well washed with hot water. The filtered liquid now contains the alkalies only, with a trace of silver, which is removed by muriatic acid. The amount of these is estimated in the usual manner. The precipitate is digested with hydrochloric acid, and after the separation of the chloride of silver, the magnesia is precipitated by phosphate of soda and ammonia.

The carbonate of silver is preferred to the acetate or nitrate in these analytical operations, in consequence of affording insoluble magnesia at

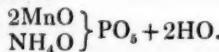
\* Ann der Chem. und Pharm. LXVI. 280.

† Pogg. Ann. LXXIV. 313.

once from the chloride, which would not be obtained by the use of the other salts. The carbonate may be most advantageously prepared for this purpose by precipitating the nitrate with carbonate of ammonia; and it is desirable not to dry the carbonate after it has been thoroughly washed.

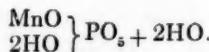
*On the separation of antimony from arsenic.\**—The method of separation recommended in this paper by Meyer, is founded upon the entire insolubility of antimoniate of soda, and upon the conversion of antimony containing arsenic into arseniate and antimoniate of soda. The author satisfied himself of the complete insolubility of the antimoniate by a series of experiments, and recommends the following process for obtaining chemically pure antimony. Commercial antimony is pulverized and heated to redness with  $1\frac{1}{4}$  of crude nitrate of soda and  $\frac{1}{2}$  of carbonate of soda. The fused product is treated with water. The residual antimoniate of soda, melted with half its weight of cream of tartar, yields a brilliant regulus of pure antimony.

*On the combinations of ordinary phosphoric acid with protoxide of manganese.†*—One only of the compounds which phosphoric acid forms with the protoxide of manganese is known at present, and into the constitution of this ammonia likewise enters. According to Otto's analysis, this salt is represented by the formula :



The precipitate produced by phosphate of soda in protosulphate of manganese is assumed by Berzelius, from analogy to the other phosphates, to be composed of  $2\text{MnO}$ ,  $\text{PO}_5$ . This formula, however, according to the experiments of W. Heintz, does not express the composition of the compound.

When the phosphate of the deutoxide of manganese is strongly heated, the deutoxide of the metal is reduced to protoxide, and the residue is soluble in water, the solution yielding crystals when evaporated to the consistence of a syrup. The same crystals are obtained by dissolving in phosphoric acid the precipitate produced by phosphate of soda in a proto-salt of manganese. This compound is an acid salt, and is represented by the formula :



It is soluble in water, but insoluble in alcohol, which latter substance rapidly removes a part of the phosphoric acid at the boiling temperature, leaving a compound containing 2 atoms of base to one of phosphoric acid.

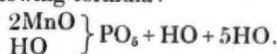
The salt precipitated by an excess of phosphate of soda from protosulphate of manganese was found composed according to the formula :



\* Ann. der Chem. und Pharm. LXVI. 236.

† Pogg. Ann. LXXIV. 449.

Phosphate of manganese, containing two atoms of fixed base was obtained by acidifying a solution of the phosphate of manganese with acetic acid, and adding phosphate of soda to the solution until the precipitate, which at first is re-dissolved, becomes permanent, and manganese yet remains in solution. The precipitate is at first amorphous, but gradually becomes crystalline, and the filtrate likewise deposits small crystals of the composition expressed by the following formula :



*On the combinations of sesquioxide of manganese.\**—Our knowledge of the salts of the deutoxide of manganese is confined to the double salts into which the sulphate of this base enters with sulphate of potash, and to a salt of phosphoric acid, which is produced, according to Gmelin, when the peroxide of manganese is heated to redness with an excess of phosphoric acid. A peach-coloured powder is left on treating the fused mass with water, which is insoluble, and deposits brown oxide of manganese on the addition of potash. Gmelin considers this body to be metaphosphate of the deutoxide; it has not, however, been analysed, but is probably the substance which colours the bead of microcosmic salt in the outer flame produced by the blow-pipe. Fromberg has also asserted that the deutoxide of manganese is dissolved by concentrated tartaric acid, and that the solution thus obtained is not precipitated by potash. R. Hermann has endeavoured to obtain salts of this oxide by preparing, in the first instance, the pure substance. This he obtained from the protosulphate, by decomposition with nitrate of barytes, evaporating the solution to dryness and heating at a low temperature until the whole of the nitric acid was expelled. Pure deutoxide he obtained, with certain precautions, by this means, but his endeavours to unite it with acids without decomposition, were unsuccessful. The deutoxide was therefore employed in preparing the phosphate. Phosphoric acid was evaporated with this oxide, and the residue was heated to a temperature somewhat below a red heat. The violet-coloured mass thus obtained, dissolved partially in water, leaving a peach-coloured residue. The solution deposited light brown red crystals, which were easily washed, but were obviously a mixture, as black spots were observed in different parts, probably consisting of peroxide of manganese. The analysis of the peach-coloured powder yielded the following formula :



With a view to obtain combinations of the deutoxide with organic acids, pure deutoxide was prepared by treating the protosulphate with sal-ammoniac in water, to which a large excess of ammonia was added. Hydrated sesquioxide was gradually deposited from the solution by the action of the atmospheric oxygen; a current of air passed through the solution, accelerated

\* Pogg Ann. LXXIV. 303.

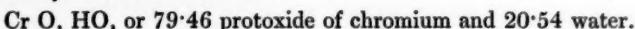
the deposition. The hydrate is dissolved by concentrated tartaric acid, and a dark brown solution obtained, which, however, after the lapse of twenty-four hours, becomes perfectly colourless, and deposits a crystalline salt. This salt the author found to consist of tartrate of the protoxide. On examining the products of this reaction, it was found that carbonic acid was evolved, and a smell of formic acid was observed. Oxalic and malic acids likewise yielded salts of the protoxide, when treated in the same manner with the hydrated deutoxide of manganese, and carbonic acid was simultaneously liberated. The volatile organic acids have no reaction on the hydrated deutoxide, and a similar negative result was obtained with benzoic and hippuric acids.

*On protoxide of chromium.\**—Berzelius fixed the atomic weight of chromium at 351·819, but this number was objected to by Peligot in the year 1844, and from the analyses of the chloride of chromium and the acetate of the protoxide, numbers were obtained varying between 325 and 330. Berlin subsequently proposed 328·389 as the more correct atomic weight of this metal. Moberg, by analyzing some of the salts of chromium, which are decomposed at a strong red heat, has endeavoured to establish this point with still greater certainty. The analyses of the sulphate of chromium and ammonia, which appeared liable, experimentally, to the least objection, gave as the mean, the number 334·87 as the atomic weight of the metal.

The analyses of chrome iron ore and pyrop have led the author to assume the presence of protoxide of chromium in these minerals.

Protoxide of chromium was obtained as a hydrate from the protochloride by introducing potash into the solution over mercury, the air being carefully excluded, which converts it immediately into green oxide. The protoxide is of a brown colour, and having been washed with boiled water, in an apparatus constructed for the exclusion of air, was dried in a current of hydrogen gas. The dry powder is of a dark brown colour, is slowly soluble in concentrated acid, without the aid of heat; in dilute acids, it is scarcely soluble. The solution soon becomes green from the formation of the oxide, and metallic chromium is deposited. The protoxide appears to undergo no change when preserved in the dry state in the air.

The analysis led to the formula :



When heated to redness, it is decomposed, the oxygen of the water combining with the protoxide, and converting it into the oxide of chromium.

The salts of the protoxide of chromium described in the author's second memoir were obtained from the protochloride, which had been prepared from the chloride by a current of the purest hydrogen gas, dissolved in water without access of air, and precipitated with solutions of potash or soda-

\* Journ. für prakt. Chem. XLIII. 114, and XLIV. 322.

salts, also free from air ; and the precipitates were also washed without exposure to the atmosphere.

No precipitate is obtained in solutions of protochloride of chromium by bromide, iodide or sulphocyanide of potassium. Fluoride of potassium produces a greenish powder. The attempts at obtaining a combination of the protoxide with sulphuric acid were unsuccessful.

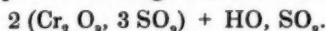
With salts of sulphurous, phosphoric, boracic, carbonic, oxalic and formic acids, amorphous precipitates, mostly of a blue colour, were obtained. A warm solution of acetate of soda alone produced a crystalline precipitate on cooling, the crystals in the moist state were quickly decomposed by exposure to the air, into a green powder soluble in water. They were more stable when dry, and could be preserved in a bottle filled with carbonic acid gas. The analysis of these crystals yielded the formula :



The succinate of protoxide of chromium had a similar composition ; the benzoate was anhydrous. The citrate was the least stable of all the salts, its solution being rapidly resolved into a dark green liquid, while carbonic acid escaped.

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*On some combinations of chromium.\**—Traube has re-examined several compounds of chromium, the composition of several of which has been heretofore erroneously stated, in consequence of impurities in the substances which were operated upon. Amongst these are the *insoluble red sulphate of chromium* obtained by the action of strong sulphuric acid with the agency of heat, upon pure oxide of chromium, bichromate of potash, chromic acid, or chrome-alum. The reddish grey substance resulting from this reaction was composed according to the formula :



A compound of oxide of iron and alumina, similar to the insoluble sulphate of oxide of chromium could not be obtained.

The products of the action of concentrated sulphuric acid upon bichromate of potash vary in composition with the temperature at which the reaction ensues and the time during which it lasts ; several compounds, containing different amounts of sulphate of potash, were obtained, which were all converted into the insoluble sulphate of chromium by the prolonged action of the acid.

The action of concentrated sulphuric acid on chrome-alum, was stated by Hertwig to yield anhydrous chrome-alum ; the author finds that the same products are obtained in this case as from the bichromate of potash, but that the quantity of sulphuric acid used here determines their composition, and not the temperature at which the reaction occurs.

Sulphuretted hydrogen gas, passed over red hot sulphate of chromium, gives rise to a deposition of sulphur, sulphurous acid and water being

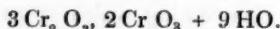
\* Ann. der Chem. und Pharm. LXVI. 87.

evolved, while sulphuret of chromium remains. This latter is a black powder, which is converted into oxide of chromium when heated in a current of oxygen gas.

A current of hydrogen gas, passed over the insoluble sulphate of chromium at a red heat, is stated by Schrötter to afford water, sulphuretted hydrogen, and sulphur, while oxide of chromium remains. On the other hand, E. Kopp affirms that water, sulphurous acid, and a brownish black powder result from this reaction, the latter of which is composed of  $\text{Cr}_4\text{S}_2$ , and is a most energetic pyrophorus. The author's experiments tend to show that the product from this reaction is not of uniform composition, but consists of a mixture of proto-sulphide with oxide of chromium, the volatile product consisting of water, sulphur, sulphurous acid, and lastly of sulphuretted hydrogen.

Dry chromic acid was treated with sulphurous acid gas, in the hopes of obtaining neutral anhydrous sulphate of chromium. At the temperature of 100° C. (212° F.) and below, the sulphurous acid exerted no action on the chromic acid; at a temperature of 210° (230° F.), in an oil-bath, the chromic acid was very slowly decomposed, and only on the surface, into a black substance, which had the properties of chromate of oxide of chromium, but likewise contained a small quantity of sulphuric acid, the formation of which was attributed to the presence of a trace of water. It appears, therefore, that sulphurous acid does not convert dry chromic acid into the sulphate of chromium, but into chromate of the oxide, with the evolution of anhydrous sulphuric acid.

Anhydrous chromate of oxide of chromium is obtained by heating chromic acid to a temperature somewhat above 250° C. (482° F.). Oxygen is then evolved, and a black substance remains, which is composed according to the formula  $\text{Cr}_2\text{O}_3$ ,  $3\text{CrO}_3$ , and which is converted by boiling water from an insoluble into a soluble modification. The reduction of chromic acid by means of alcohol, yielded a hydrated chromate of oxide of chromium, which is identical with that obtained by Rammelsberg, on mixing solutions of neutral chromate of potash and chrome-alum, and the formula for which is :



Traube has likewise found,\* that at least  $9\frac{1}{2}$  to  $12\frac{1}{2}$  parts of concentrated sulphuric acid are required to precipitate, free from bisulphate of potash, the chromic acid contained in 1 part of bichromate of potash dissolved in  $4\frac{1}{2}$  or  $5\frac{1}{2}$  parts of water. An excess of sulphuric acid above that quantity, however, tends to the production of larger crystals.

In preparing the acid, he recommends that 1 part of bichromate of potash should be warmed with  $3\frac{1}{2}$  parts of sulphuric acid and  $2\frac{1}{2}$  parts of water. The greater part of the potash is then separated, when the liquid cools, in the form of bisulphate of potash. To the liquid poured off from these crystals, 4 additional parts of sulphuric acid are added, which precipitate chromic

\* Ann. der Chem. und Pharm. LXVI. 165.

acid. The whole is then warmed, and with the addition of water to dissolve the acid, when the solution is evaporated until a crystalline crust appears on the surface. On cooling, crystals of chromic acid are obtained. These are purified by careful fusion in an air-bath, re-solution, evaporation, and crystallization, or by solution in water, to which sulphuric acid is added until the chromic acid begins to deposit ; the solution is then evaporated until a crust appears on the surface, when it is placed in a cool position, to allow the crystals to form. The crystals are dried upon a porous tile, and then recrystallized from water.

*Blue* sulphate of oxide of chromium was obtained by dissolving 1 part of chromic acid in  $1\frac{1}{2}$  parts of concentrated sulphuric acid, and  $2\frac{1}{4}$  parts of water ; the solution was exposed in a shallow dish to the vapour of ether, from a crucible containing liquid ether, placed in the centre of the dish. In a few hours nearly the whole liquid solidified to a mass of small crystals of the blue sulphate. The reduction is completed by a few drops of alcohol.

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*On some of the combinations and on the atomic weight of molybdenum.\*—* From the time that Scheele first discovered the real composition of the mineral sulphuret of molybdenum, very little progress was made in the study of the combinations of this metal until Berzelius determined its atomic weight, and in 1825, established the definite nature of its three oxygen compounds and investigated its sulphur salts. Messrs. Svanberg and Struve have now examined several of the salts of the acid, its relations to phosphoric acid, and have determined its atomic weight with greater accuracy.

For the preparation of molybdic acid, the sulphuret of molybdenum from Lindås, in Småland, in Sweden, was roasted in the state of a fine powder, in a clay vessel, over a charcoal fire, with constant agitation. The powder acquires a yellow colour and cakes together on the dish. It is then treated with ammonia in a close vessel, when the whole of the molybdic acid is dissolved. The insoluble residue must be repeatedly roasted, and again treated with ammonia, in order to convert it entirely into molybdic acid. The ammoniacal solution still retains small portions of alumina, oxide of copper, and phosphoric acid ; to remove these, it is mixed with carbonate of potash and evaporated, a portion of the alumina then subsides, and is separated by filtration. The clear liquid is evaporated to dryness and heated to redness in a platinum crucible. The fused mass treated with water, yields a solution of molybdate, sulphate, and phosphate of potash, while alumina and oxide of copper remain insoluble. The filtered solution of the salts of potash is again evaporated to dryness, the dry mass mixed with twice its weight of sulphur, and heated to redness in a porcelain crucible or a glass matrass, which admits of being closed by a stopper. The mass being cooled, is treated with water, which leaves a blackish-green insoluble substance ; this is again washed with hot water, and subsequently boiled with

\* Jour. für prack. Chem. XLIV. 257.

a little carbonate of potash, which operations are repeated until the liquid is no longer yellow, deposits no sulphur when an acid is added to it, and evolves no sulphuretted hydrogen. All the excess of sulphur, and the whole of the phosphoric acid are thus removed from the sulphuret of molybdenum, which is now washed with water containing hydrochloric acid, and lastly with pure water. The sulphuret is now pure, and may be roasted or treated with nitric acid, in order to convert it into molybdic acid. When heated in a platinum capsule, exposed to the air, the acid should leave no fixed residue.

This circuitous process for obtaining the pure acid is not essential in the preparation of all the salts.

The salts which have been fully described and analyzed by the authors, are the following :

*Neutral molybdate of potash* (dried over sulphuric acid)  $\text{K}_2\text{O}, \text{MO}_3 + \frac{1}{2}\text{HO}$ .

*Bimolybdate of potash* was not obtained.

*Double salt of bimolybdate of potash with trimolybdate of potash,*  $3 [\text{K}_2\text{O}_2, (\text{MO}_3)] + \text{K}_2\text{O}, 3 \text{MO}_3 + 6 \text{HO}$ .

*Trimolybdate of potash*, salt dried in the air,  $\text{K}_2\text{O}, 3 \text{MO}_3 + 3 \text{HO}$ .

*Molybdate of potash with 4 atoms of acid*,  $\text{K}_2\text{O}, 4 \text{MO}_3$ .

*Molybdate of potash with 5 atoms of acid*,  $\text{K}_2\text{O}, 5 \text{MO}_3$ .

Three other salts of potash were observed, but not minutely examined.

*Neutral molybdate of soda*,  $\text{Na}_2\text{O}, \text{MO}_3 + 2 \text{HO}$ .

*Bimolybdate of soda*,  $\text{Na}_2\text{O}, 2 \text{MO}_3 + \text{HO}$ .

*Trimolybdate of soda*,  $\text{Na}_2\text{O}, 3 \text{MO}_3 + 5 \text{HO}$ .

*Neutral molybdate of oxide of ammonium*,  $\text{NH}_4\text{O}, \text{MO}_3$ .

*Bimolybdate of oxide of ammonium*,  $\text{NH}_4\text{O}, 2 \text{MO}_3$ .

*Double salt of bimolybdate and trimolybdate of oxide of ammonium*,  $\text{NH}_4\text{O}, 2 \text{MO}_3 + \text{NH}_4\text{O}, 3 \text{MO}_3 + 3 \text{HO}$ .

Molybdic acid forms numerous salts with barytes, but these are very difficultly separated from small quantities of the potash or ammonia salts, from the decomposition of which they are produced. The acid salts, of which there are many, are all crystalline. The neutral and bimolybdates of barytes were analysed, the former being found identical with the salt described as basic by Heine; also a double salt, of the following composition,  $\text{BaO}, 2 \text{MO}_3 + \text{BaO}, 3 \text{MO}_3 + 6 \text{HO}$ , and a salt containing 9 atoms of acid,  $\text{BaO}, 9 \text{MO}_3 + 4 \text{HO}$ , obtained by treating the neutral salt with dilute nitric acid.

The neutral salts of lead and silver, and an acid salt of the latter, corresponding with the formula  $\text{Ag}_2\text{O}, 3 \text{MO}_3 + \text{Ag}_2\text{O}, 2 \text{MO}_3$  were likewise examined.

*Combination of molybdic and phosphoric acids*.—Amongst other facts connected with the mutual reaction of these two acids, Berzelius states, that when an excess of molybdic acid is digested with phosphoric acid, the latter is precipitated and forms a lemon-yellow coloured powder with the molybdic acid, which resembles a basic salt and is insoluble in water.

The authors prepared this substance in larger quantity by dissolving molybdic acid in an excess of ammonia, and adding a few drops of phosphate of soda to the solution, which is then heated with an addition of nitric acid. A yellow powder is instantly precipitated, which is insoluble in water and acids, but appears upon analysis to contain very little phosphoric acid, and to be chiefly composed of the acid salt,  $\text{NH}_4\text{O}_5\text{MO}_3$ . Similar salts of potash and barytes were obtained from the ammoniacal compound, all containing small and variable quantities of phosphoric acid. These yellow salts could never be obtained with pure molybdic acid, but the tendency which small quantities of phosphoric acid exhibit to combine with molybdic acid is so great, and the yellow colour of the compounds is so characteristic, that the authors recommend the molybdate of ammonia as a qualitative test for minute quantities of phosphoric acid.

*Determination of the atomic weight of molybdenum.*—Berzelius ascertained the atomic weight of this metal in 1818, by precipitating a known quantity of nitrate of lead with neutral molybdate of oxide of ammonium, and calculated the result from the amount of molybdate of lead which he obtained. Far from considering the method employed as accurate, Berzelius himself, in the last edition of his "Lehrbuch," calls upon others to adopt other means for ascertaining this point, some of which he himself points out.

Svanberg and Struve have detailed at length the different methods employed by them for effecting this object. It would exceed our limits to do more than name them.

1st. Molybdic acid was reduced by pure hydrogen gas to the lowest oxide of the metal, 2 atoms of  $\text{MO}_3$  yielding  $\text{M}_2\text{O}_3$ ; but the acid could not be converted into metal. The heat necessary for this partial reduction, and the length of time required, materially affected the glass vessels in which the operations were performed, and tended to render the results inaccurate.

2nd. The conversion of molybdic acid into sulphuret of molybdenum, by means of a current of sulphuretted hydrogen gas, gave no better results. An oxysulphuret was produced, which could only be decomposed completely with the greatest difficulty, and no two experiments agreed.

3rd. Neutral molybdate of potash, treated with sulphuretted hydrogen gas, gave rise to a copious formation of water; but when this had ceased and the heated product was gradually allowed to cool, at a certain temperature, a complete absorption of the sulphuretted hydrogen by the metallic sulphurets was observed, which lasted for a short period. The absorption of the gas in this manner would of course give rise to error, and an attempt was made to expel it by carbonic acid gas, but without success. Dry air, employed for the same purpose, answered better, but the results even then could not be depended upon.

4th. Trimolybdate of potash was also submitted to the action of dry sulphuretted hydrogen. On the application of heat, water and sulphur were evolved. A triple sulphuret was consequently not obtained, but a

bisulphuret of molybdenum and a higher sulphuret of potassium; the result in this case was also of too complicated a nature to be employed as a means of determining the atomic weight of molybdic acid.

5th. Experiments to ascertain the atomic weight of molybdenum by the fusion of carbonates of the alkalies with molybdic acid. A neutral salt of molybdic acid resulting in these experiments from the fusion, the atomic weight was calculated from the amount of carbonic acid expelled from the alkaline carbonate. The results agreed very well with the atomic weight obtained by a subsequent method; but as they did not tally well with each other, no great reliance could be placed upon the method.

6th. Experiments undertaken with the chlorides were unsuccessful, the production of pure salts being very difficult, and the accurate estimation of the chlorine in the compounds by means of silver, being found totally impracticable.

7th. The most accurate results were obtained by roasting pure artificial dry sulphuret of molybdenum in a glass tube, exposed to a current of air, and estimating the quantity of molybdic acid resulting from this operation. The atomic weight of molybdenum, calculated from the result of these experiments, will be dependant upon the atomic weight of sulphur, which, according to Berzelius, is 200.75, and, according to Erdmann and Mar-chand, 200.00. The first of these numbers gives :

588.966 as the atomic weight of molybdenum, and the second  
575.829.

The authors are in favour of the lower number, because it is more in accordance with all the results of the different series of experiments.

*Contributions to the knowledge of the slags from iron furnaces.\**—It is well known, and has lately attracted much attention, from the experiments of Dr. Percy, that the slag from different metallurgical operations frequently occurs as an amorphous vitreous mass, enclosing crystalline particles, and sometimes even well-formed crystals. It has been supposed that these crystals were distinct compounds that had separated from a mixture of the silicates in the amorphous mass, as a well-defined salt will sometimes separate from a solution of other salts. On the other hand, it has been assumed that the crystals were of the same composition as the matrix in which they occur, and only differed in possessing symmetrical proportions. With a view to ascertain the relations of composition between the amorphous and crystalline varieties of slag, Rammelsberg has analysed a series of both kinds from different iron furnaces in Germany, and the general conclusions at which he arrives are, that the amorphous and crystalline slags have essentially the same chemical composition. The specific gravity of the two kinds is also the same, which would not have been anticipated from the different manner in which their molecules are arranged.

\* Pogg. Ann. LXXIV. 303.

*On the effect of time in the production of chemical compounds.*\*—Liebig in illustrating this subject, calls attention to the conversion of a concentrated solution of oxalic acid in alcohol into oxalic ether and oxaloinic acid, when kept at a temperature of 40° or 50° C. (104° to 122° F.) for several months. A like effect is produced in an alcoholic solution of hippuric acid under the same circumstances, hippuric ether being formed. Other acids, like the benzoic, require the agency of hydrochloric acid in effecting these changes, in which case chlorine compounds are first produced, which, like the nitric oxide in the process for sulphuric acid, probably, act as mediating agents in the conversion. The formation of acetic ether and cenanthic ether in stored wines, appears due to the same cause.

*On neutral sulphate of ethyl, and its products of decomposition with water.*†—The only compound of sulphuric acid and ethyl yet described is the acid sulphate, or as it is more generally termed, sulphovinic acid. Wetherill has obtained the neutral salt by exposing anhydrous ether, or absolute alcohol, to the vapours of anhydrous sulphuric acid, the vessel in which the absorption is conducted being cooled by a freezing mixture. The liquid separates into two strata, the upper of which contains the neutral sulphate of ethyl, which is purified from sulphurous acid by agitation with milk of lime, washed with water, and then separated from an excess of ether by distillation. An oily liquid is thus obtained, which still possesses a faintly acid reaction. This is again washed with water, the last portions of which are removed with blotting-paper, and the product is then dried over sulphuric acid in vacuo.

The neutral sulphate is an oily liquid, possessing a sharp taste, and causing a burning sensation in the throat. Its smell resembles that of peppermint. On paper a fatty spot is produced by the oil, which, however, rapidly disappears. The specific gravity of the oil is 1.120. It is colourless when pure, but generally has a yellow tint. It can only be distilled with difficulty without decomposition, a current of carbonic acid gas being passed through the liquid in a shallow retort. Oily drops pass over at 110—120° C. (230—248° F.); if the temperature rises to between 130—140° C. (266—284° F.) decomposition ensues, the liquid becomes black; sulphurous acid and alcohol are evolved, and if the temperature be raised still higher these are accompanied by olefiant gas. The distillate is neutral, colourless, and heavier than water. The liquid is not decomposed by chlorine in the cold, but the gas is absorbed, and imparts a greenish colour to the solution. Sulphuretted hydrogen does not react upon the neutral sulphate, but hydrosulphuret of sulphuret of potassium converts it into mercaptan, and sulphate of potash. The composition of the substance, ascertained by analysis, verified its theoretical formula:



\* Ann. der Chem. und Pharm. Lxv. 350.

† Ibid. LXVI, 117.

When the neutral sulphate of ethyl is heated and agitated with water the oil entirely dissolves, and a very acid solution is obtained, which affords alcohol on boiling. Treated with an excess of barytes, three salts of that base are obtained in solution. The first of these, which separates in crystalline plates on the addition of alcohol, or by slow evaporation, is the methionate of barytes,  $C_2 H_3 S_2 O_7 \cdot BaO$ . The mother-liquor contains a mixture of two salts, the sulphovinate and isæthionate of barytes.

The action of anhydrous sulphuric acid upon ether gives rise, therefore, to the production of neutral sulphate of ethyl; but a portion of the sulphuric acid withdraws the elements of water from another portion of ether, so that, on the one hand, the compound of Regnault,  $4 SO_3 \cdot C_4 H_4$ , on the other, sulphovinic ( $C_4 H_5 O \cdot HO \cdot 2 SO_3$ ), and methionic acids, ( $2 SO_3 \cdot C_4 H_5 O \cdot HO$ ), are produced, which always accompany the production of the neutral sulphate.

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*On the action of acids on amygdalin.\**—Wöhler has investigated the action of hydrochloric acid upon amygdalin, the products from which are no doubt similar to those that would be obtained with any of the stronger acids.

A solution of amygdalin, treated with fuming hydrochloric acid, becomes yellow on the application of heat, and a large quantity of a brownish-black powder, resembling humin, is deposited when the temperature is still further increased.

The brown liquid, filtered from the humin, when evaporated in a water bath, leaves a syrupy mass, which consists of a mixture of humic acid, sal-ammoniac, and formo-benzoic acid. Ether extracts the latter, which may be thus obtained in tabular rhombohedrons. If the acid liquid acquires a higher temperature than  $100^\circ C.$  ( $212^\circ F.$ ) during evaporation, a portion of the formo-benzoic acid undergoes a change; it becomes amorphous, and although it is soluble in a small proportion of water, is precipitated by a larger quantity in the form of a heavy, yellow inodorous oil.

With a view of obtaining the unknown ether of formo-benzoic acid, hydrochloric acid gas was conducted into a thick solution of amygdalin in alcohol; the amygdalin gradually dissolved as the gas was absorbed, and was not again precipitated when the liquid cooled. After standing for some days, pulverulent sal-ammoniac separated, and was increased in quantity by the addition of ether. A still further addition of ether caused the separation of an aqueous acid liquid, which contained the whole of the sal-ammoniac, but no sugar. This having been repeatedly shaken with ether, the etherial solution was drawn off, and on removing the ether by distillation, a brown syrup remained, which sunk in water. It is this body that in all probability, is the ether of amygdalonic acid, produced by the sugar, or gum, in amygdalin, uniting with formo-benzoic acid, instead

\* Ann. der Chem. und Pharm. lxvi, 238.

or being converted into humin. For amygdalinic acid is composed of,  $\text{HO} + \text{C}_{40}\text{H}_{26}\text{O}_{21}$ , and may be viewed as a combination of :

1 equiv. oil of bitter almonds	$\text{C}_{14}\text{H}_6\text{O}_2$ .
1 " formic acid . . .	$\text{C}_2\text{H}\text{O}_3$ .
2 " sugar . . . .	$\text{C}_{24}\text{H}_{20}\text{O}_{20}$ .

The ether of amygdalinic acid is, doubtless, colourless in the pure state. Obtained as described above, it is light brown, heavier than water, and not mixible with, but soluble to a considerable extent in it, particularly when heated. Heat, however, partially decomposes the ether. It possesses a bitter, somewhat astringent taste. This ether is not volatile, or very partially so, without undergoing decomposition.

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*On pyrotartaric acid.\**—The composition of this acid has long been a matter of controversy among those who have occupied themselves with its study. Different experimenters accord it the three following different formulæ :  $\text{C}_4\text{H}_5\text{O}_4$ , Göbel;  $\text{C}_4\text{H}_4\text{O}_4$ , Gruner;  $\text{C}_6\text{H}_8\text{O}_3$ , Pelouze; the published descriptions of its salts are likewise not in accordance. Arppe has consequently re-investigated the subject.

The acid was prepared upon the plan recommended by Millon and Reiset, by distilling pulverized tartaric acid mixed with pumice-stone. Carbonic acid, water, acetic acid and pyrogenous oil accompany the distillate of pyrotartaric acid. The crude product is treated with water, and the oil separated by a wet filter, the filtrate evaporated at a moderate temperature and allowed to crystallize. A highly coloured crystalline mass is thus obtained, which is spread out upon a thick layer of blotting-paper and exposed under a large bell-jar to the vapours spontaneously evolved from a series of vessels containing alcohol; the alcoholic vapours dissolve out the residue of pyrogenous oil, which is then absorbed by the bibulous paper. The acid, which is still impure, is dissolved in water, and treated with nitric acid at a slightly elevated temperature, and the solution then evaporated to the point of crystallization. The acid is thus obtained so pure, that it simply requires fusion, to expel the nitric acid, and become perfectly colourless and without smell. The produce amounts to about 7 per cent of the tartaric acid employed. The analysis of the acid and of the silver-salt led to the formula established by Pelouze for the crystallized acid :



The distillation of the crystalline acid with anhydrous phosphoric acid yielded anhydrous pyrotartaric acid, which condensed in the form of an oily liquid. This oil is colourless, and at a temperature of  $20^\circ\text{ C.}$  ( $68^\circ\text{ F.}$ ) is without smell; at a temperature of  $40^\circ\text{ C.}$  ( $104^\circ\text{ F.}$ ), however, it acquires the odour of acetic acid. Its taste is first sweet, afterwards sharp, and lastly sour. The acid is heavier than water; at  $-10^\circ\text{ C.}$

\* Ann. der Chem. und Pharm. LXVI. 73.

(14° F.) it is still liquid ; it boils at 230° C. (446° F.), and is volatilized without serious decomposition ; it is perfectly neutral, dissolves easily in alcohol, and is precipitated in the form of oily drops by water, which however gradually disappear, and are converted into ordinary pyrotartaric acid. The analysis of this substance confirmed its anhydrous condition, and left no doubt regarding its constitution. A series of the salts of pyrotartaric acid were likewise examined by the author.

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*On the differences between lactic acid produced by the fermentation of sugar and that contained in the juices of flesh.\**—Liebig remarks, in his treatise on the juices of flesh, that the zinc and lime-salts of the lactic acid obtained from that source, did not contain the same amount of water as the salts of the same acid obtained and described by Messrs. Engelhardt and Maddrell in their paper on lactic acid, produced from the fermentation of sugar. Engelhardt has investigated this difference in the salts obtained from the acids of different origin, and considers that there exist either two modifications of the compound  $C_6 H_6 O_6$ , or that the acid must be both mono- and bibasic.

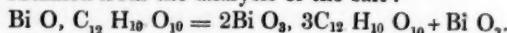
The lime and magnesia salts of the acid from flesh contained 4 equivs. of water, whereas the lime-salt of the acid produced from sugar contained 5 equivs., and the magnesia salt only 3 equivs. of water. The relation of solubility and the outward appearance of the salts also indicated an obvious difference in their nature.

The acid of flesh produces a salt with zinc containing 2, while that from sugar contains 5 equivs. of water. The water in these salts is also separated with different degrees of facility, and the salts themselves are decomposed at very distant temperatures.

The copper-salts of the two acids, are also palpably distinct, and do not admit of the acids being considered identical. The existence of a basic zinc-salt of the acid procured from sauerkraut appears also in favour of the existence of two isomeric acids, as no similar compound could be obtained from the acid derived from sugar.

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*On lactate of bismuth.†*—M. Engelhardt has prepared this lactate by mixing nitrate of bismuth with an excess of a concentrated solution of lactate of soda. The mass of crystals, containing in the first instance cubic nitre, is dissolved in water and set aside to deposit crystals : the mother-liquor affords an additional crop by the consecutive addition of small quantities of alcohol and spontaneous evaporation. The following formula was obtained from the analysis of the salt :



If the solutions are mixed warm, or if nitrate of bismuth is dropped into a moderately dilute solution, the latter being in excess, and the whole is then

\* Ann. der Chem. und Pharm. Lxv. 359.

† Idem, Lxv. 367.

boiled, a pulverulent precipitate is obtained, which has the composition expressed by the following formula :



*On some products of the decomposition of chrysammic acid.\**—Dr. Schunk published an account some years ago of the action of nitric acid upon aloes, in which he described three new acids as the resulting products of this reaction. He now finds, that only two of these acids, the chrysammic and aloetic, are peculiar to the reaction of nitric acid upon aloes, and that the aloeresinic is the product of the decomposition of chrysammic acid, while chrysolepinic acid, which is also obtained at the same time, is now found to be identical with carbazotic acid, some of its properties being masked by an admixture of the other acids.

Aloetic acid can also be completely converted into chrysammic acid, by the continued action of nitric acid, but the latter is perfectly persistent when treated with the fuming acid.

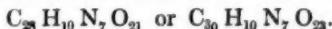
The analysis of aloetic acid assigns it the formula :



and by the oxidation and removal of 1 equiv. of carbon and 2 equivs. of hydrogen, it becomes converted into chrysammic acid.

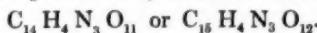


When chrysammic acid is boiled with an aqueous solution of ammonia, the acid is dissolved and a purple liquid formed, which deposits crystalline needles when allowed to cool. These crystals are not chrysammate of ammonia, for no chrysammic acid is precipitated on treating a solution of them with a mineral acid. The crystals are indeed an amide, which Schunk calls *chrysamminamide*, and are constituted as follows, the analysis agreeing equally well with both formulæ :



Chrysamminamide is consequently produced by the substitution of 3 equivs. of amidogen for 3 equivs. of oxygen in 2 equivs. of chrysammic acid.

When dilute sulphuric acid or hydrochloric acid is added to a solution of chrysamminamide in water, dark needles are deposited when the liquid cools, which when washed, are of a dark olive-green colour. The substance thus obtained is an acid, called by Schunk, *amido-chrysammic acid*, and its composition is represented by either of the two following formulæ :



A red crystalline salt of barytes is produced by the addition of chloride of barium to a solution of the acid in ammonia.

1 equiv. of chrysamminamide is consequently converted by weak acids into 2 equivs. of amido-chrysammic acid, by the assumption of 1 equiv. of water and the simultaneous separation of 1 equiv. of ammonia.

\* Ann. der Chem. und Pharm. Lxv. 234.

Amido-chrysammic acid is converted into chrysammic acid by boiling nitric acid, with the evolution of ruddy fumes, and nitrate of ammonia is obtained on evaporating the liquid; the same conversion is effected by concentrated, but not by dilute, sulphuric acid. Ammonia is evolved when this acid is treated with potash, and chrysammic acid probably generated.

The salts of amido-chrysammic acid present the same outward appearance and properties as those of chrysammic acid; they detonate also in a similar manner. They are, however, easily distinguished by the evolution of ammonia when heated with potash.

The insoluble salts may be prepared by double decomposition with amido-chrysammate of potash, or with chrysamminamide to which ammonia has been added; chloride of barium decomposed chrysamminamide on continued boiling, without the intervention of ammonia, and amido-chrysammate of barytes was produced.

When chrysammic acid is treated with caustic potash, 3 equivs. of carbonic acid are separated and 3 equivs. of water entering into the compound, an acid is produced, which the author believes to be the aloeresinic acid noticed in his first memoir.

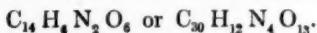
Chrysammic acid =  $C_{15}H_2N_2O_{13}$  —  $3CO_2 + 3HO = C_{12}H_5N_2O_{10}$ , which is the formula for aloeresinic acid deduced from the analysis of the barytes salt. This acid is never produced when carbonate of potash is used instead of caustic potash in the preparation of chrysammic acid from aloes.

Chrysammic acid dissolves with a deep blue colour, in a boiling solution of sulphuret of potassium containing an excess of caustic potash, and when the liquid cools, a mass of crystalline needles separate, which when washed and dried, are of an intense indigo-blue colour. This is a new body, called by the author *hydrochrysammide*. To purify the substance, it is recrystallized from a solution in potash, none of which substance, however, enters into its composition. This body is completely dissipated when heated on platinum. Heated in a tube, it evolves violet vapours, which condense into crystals on the sides of the tube, but the greater part is decomposed, with the evolution of ammonia, leaving a copious residue of carbon.

Hydrochrysammide is insoluble in water, slightly soluble in boiling alcohol, to which it communicates a slight blue tint. It is soluble in concentrated sulphuric acid, but is again precipitated by water. Boiling nitric acid decomposes it. It is soluble in potash and the carbonates of the alkalies, from which solution it is precipitated by acids.

A boiling solution of protochloride of tin also converts chrysammic acid into this substance; but prepared in this manner, it is difficultly separated from oxide of tin.

The atomic weight of hydrochrysammide could not be estimated, as it does not appear to enter into definite combination. The analyses agreed with either of the two following formulæ :



1 equiv. of chrysammic acid, therefore, in losing 6 equivs. of oxygen and assuming 4 equivs. of hydrogen, yields 1 equiv. of hydrochrysammide.

The action of nitric acid on hydrochrysammide does not give rise to the formation of chrysammic acid, as might have been thought probable, but a brown pulverulent substance is produced, bearing much resemblance to aloeresinic acid, and the liquid contains ammonia and oxalic acid.

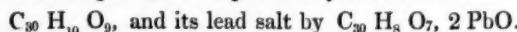
*Chemical examination of madder.\**—Debus had arrived at different results in his investigation of this colouring matter, from those obtained by Schiel and Schunck. The madder-root was boiled two or three times with fifteen or twenty times its bulk of water, and the solution having been filtered through flannel, was heated for a considerable time with hydrated oxide of lead. A portion of the lead is then dissolved, and a part forms insoluble reddish-brown compounds with the colouring matters; the liquid extract acquires a clear yellow colour, and no longer precipitates the salts of the metallic oxides. The lead precipitate, having been carefully washed, was decomposed with warm dilute sulphuric acid, when the colouring matter accompanied the sulphate of lead, and could be freed from acid by simple washing with water. On boiling this mixture several times with alcohol, the greater portion of the colouring matter is dissolved, a dark brown body remaining in an insoluble combination with the sulphate of lead. The substances held in solution by the alcohol may be distributed into two groups, the one of which is precipitable by calcined oxide of zinc, while those of the other group remain in solution; of these latter, the author gives no account at present. To obtain the former, the solution is treated with oxide of zinc as long as the oxide acquires a red colour, and heat is applied to ebullition, to cause the more rapid deposition of the compounds produced. The precipitate, after being washed with alcohol, is decomposed with sulphuric acid, which dissolves the oxide of zinc, leaving the colouring matter; the latter is purified by solution in ether, reprecipitation with oxide of zinc, and a second decomposition with sulphuric acid. The washed and purified colouring principles are then boiled with a strong solution of alum, until the alum solution deposits no solid matter when cold. The first and second portions of the solution of alum deposit a brown-red substance on cooling, which in the subsequent portions is replaced by a pure yellow deposit. This yellow body is treated with dilute hydrochloric acid, to remove the alumina which it contains, and is then obtained in beautiful yellowish-red needles, after repeated crystallization from alcohol. The crystalline substance possesses acid properties, and is called by the author, *lizaric acid*. The solution of alum, from which the lizaric acid has separated, is still of a deep red colour, and when treated with sulphuric acid deposits, after some time, another body, which may likewise be purified by solution in hot alcohol, from which

\* Ann. der Chem. und Pharm. LXVI, 351.

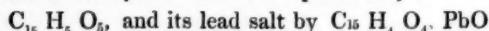
solvent it crystallizes in the cold. This latter substance is also an acid, occurring in long red needles, and is called by Debus, *oxylizaric acid*.

The yellow liquid from which the colouring matters and the oxide of lead were separated, yielded several bodies, the nature of which the author has not been able to ascertain with certainty.

Lizaric acid is identical in composition and properties, with the alizarin of Schunk. Its composition is expressed by the formula :



The composition of oxylizaric acid is expressed by :



An equiv. of lizaric acid with 1 equiv. of oxygen, therefore, afford 2 equivs. of oxylizaric acid.

The madder red, and madder purple, which have been prepared by Schiel, according to Runge's process, and analyzed, yield lizaric and oxylizaric acids on treating their solutions in alcohol with oxide of zinc.

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*On the solid, volatile, fatty acids of cocoa-nut oil.\**—Görgey has repeated Fehling's experiments upon this fat, with a view to ascertain whether capric acid could not be added to the caproic and caphylic acids discovered by the elder experimenter. He has not only succeeded in proving the presence of capric acid in this mixture of fats, but has likewise shewn that it contains lauric acid, and probably, also, myristic and palmitic acids. According to the author's investigation, and that of Fehling, cocoa-nut oil would therefore contain the following acids :

Caproic acid . . . .	$\text{C}_{12}\text{H}_{12}\text{O}_4$ .
Caprylic acid . . . .	$\text{C}_{10}\text{H}_{16}\text{O}_4$ .
Capric acid . . . .	$\text{C}_{18}\text{H}_{20}\text{O}_4$ .
Lauric acid . . . .	$\text{C}_{14}\text{H}_{24}\text{O}_4$ and probably also,
Myristic acid . . . .	$\text{C}_{16}\text{H}_{28}\text{O}_4$ and
Palmitic acid . . . .	$\text{C}_{18}\text{H}_{32}\text{O}_4$ .

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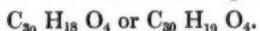
*Action of iodine on the oils of anise and fennel.†*—Dr. Will has observed, that when into a cold saturated aqueous solution of iodine in iodide of potassium, an ethereal solution of oil of anise or fennel is dropped, a thick gelatinous magma is produced, which deposits, on the addition of from six to eight times its volume of alcohol, a white pulverulent substance. With other oils of a similar nature, this reaction could not be obtained. The powder is of a brilliant white colour, not crystalline, very light and electrical. It melts at a temperature considerably above 100° C. (212° F.), and solidifies again, when cooled, into a glassy mass, exhibiting no signs of crystallization. At a higher temperature it is entirely dissipated, producing an odour resembling that of the oil of anise. The substance is

\* Ann. der Chem. und Pharm. LXVI, 290.

† Ibid. LXV. 230.

quite insoluble in water and in alcohol, but is soluble in ether, from which solution it is precipitated by alcohol. Potash, ammonia, dilute sulphuric and hydrochloric acids do not alter it, even at the boiling temperature; it is only acted upon by strong nitric acid, when boiled for a length of time with that acid. Concentrated sulphuric acid renders it of a dark brown red colour, and when warmed, a reddish solution is obtained, which again becomes colourless by dilution. Chlorine gas colours this substance of a violet hue at ordinary temperatures, the gas is absorbed, hydrochloric acid evolved, and the substance becomes warm without undergoing fusion; if the powder has been previously heated to 100° C. (212° F.), no violet colour is observed.

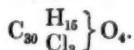
The product contains no iodine, but is represented by the formula:



It is, therefore, probably produced by the oxidizing action of iodine upon the stearopten, or solid portion of the oils. The stearopten of these oils is composed, according to Blanchet and Sell of:



with 3 equivs. of which, 1 equiv. of oxygen, according to the first formula, has entered into combination. The composition of the compound produced by chlorine upon this body, corroborates this supposition; it was found by analysis to be expressed by the formula:



*Researches into the combinations of several organic bases with hydrosulphocyanic, hydroferrocyanic and hydroferridcyanic acids.\**—The question respecting the number of atoms of carbon which enter into the constitution of one equiv. of the organic bases has been matter of dispute among several chemists, whose determinations of the carbon in these bodies, when calculated for the same atomic weight of carbon, show as great a uniformity as the methods of analysis are calculated to afford. The differences of opinion must be traced either to an uncertainty or inaccuracy in the present assumed atomic weight of carbon, or to a selection of the salts of these bases, which was not well calculated to establish correctly their atomic constitution.

The combinations of several of the vegetable bases with hydrosulphocyanic acid having been shewn by Artus, Henry and Lepage, to be insoluble and crystalline, and the hydrosulphocyanic acid being capable of accurate estimation in the form of sulphocyanide of silver, as shewn by Dr. Will, by means of nitrate of silver in a solution acidified with nitric acid, Dollfus has analysed, at the instigation of Dr. Will, a series of these compounds, with a view to establish the atomic weight and the amount of carbon in the base with greater accuracy than has hitherto been achieved.

\* Ann. der Chem. und Pharm. Lxv. 212.

The less soluble of the hydrosulphocyanates were prepared by mixing an aqueous or alcoholic solution of sulphocyanide of potassium with an aqueous or alcoholic solution of the hydrochlorate, sulphate, or nitrate of the organic base; in the case of codeine, however, and some of the other bases, a double salt is formed with the sulphocyanide of potassium, and this method of preparation cannot be followed.

Quinine appears to form two salts with hydrosulphocyanic acid, which are difficultly separated, and on this account could not be analyzed.

The analysis of the hydrosulphocyanate of morphine by means of nitrate of silver, yielded as the atomic weight of the salt the number 355, and hence is derived the number 296 as the atomic weight of morphine.

Elementary analysis yielded, in 100 parts, 60.66 carbon, 5.80 parts hydrogen, which results, in connection with the numerous analyses of pure morphine by other experimentors, and the above atomic weight, lead to the following formula for the salt :



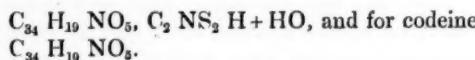
Thus the formula for morphine would be



which corresponds with the results of former analysts.

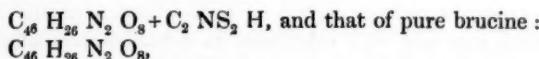
*Hydrosulphocyanate of codeine* yielded the number 294 as the atomic weight of codeine + 1 Aq.

The analysis of the salt gave carbon 62.30, hydrogen 6.13. Thus the formula for hydrosulphocyanate of codeine, calculated from the numbers of former analysts, would be :



*Hydrosulphocyanate of brucine* yielded 398 as the atomic weight of brucine.

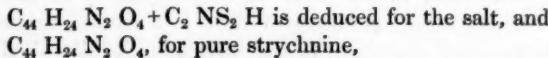
The analysis gave carbon 63.23, hydrogen 6.13. The formula for the salt is therefore :



which is in accordance with the greater number of the published analyses.

*Hydrosulphocyanate of strychnine* afforded the number 349 as the atomic weight of strychnine.

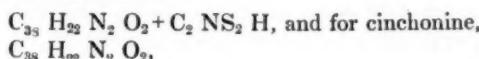
Analysis gave carbon 67.70, hydrogen 6.39. Whence the formula,



corresponding with the formula proposed by Gerhardt, but not with those of Liebig and Gmelin.

*Hydrosulphocyanate of cinchonine* gave 289 as the atomic weight of cinchonine.

Analysis yielded carbon 67.86, hydrogen 6.63 in 100 parts, and the formula for the salt would be :



which has already been proposed by Laurent, and is partially confirmed by the composition of the compounds of this base with hydroferrocyanic and hydroferridcyanic acid.

*Combination of quinine and cinchonine with hydroferrocyanic and hydroferridcyanic acids.*—When an alcoholic solution of hydroferrocyanic acid, prepared by Posselt's method, is added to an alcoholic solution of the bases, the following reactions are observed :

Quinine and cinchonine afford orange or lemon-yellow coloured crystalline precipitates, which are difficultly soluble in alcohol.

With codeine, a white precipitate is first produced, which is soluble in an excess of the acid ; when this solution is allowed to stand, small white needles are formed in the liquid. Veratrine, morphine and brucine react in a precisely similar manner, but the compounds of the latter bases are less stable, and cannot be re-crystallized. All are decomposed by the application of heat, both in solution and in the dry state, and evolve a large quantity of hydrocyanic acid, the solutions deposit at the same time white ferro-cyanide of iron, which rapidly assumes a blue colour ; the dry compounds, when heated on sheet platinum, leave a residue of pure oxide of iron.

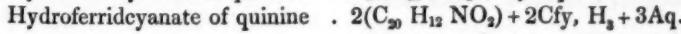
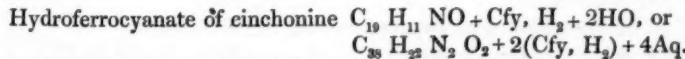
The aqueous solutions of the compounds produce the well-known reactions of hydroferrocyanic acid with the salts of iron.

The combinations of hydroferridcyanic acid with the organic bases are most readily prepared by mixing an aqueous solution of ferridcyanide of potassium with an aqueous solution of the hydrochlorate of the bases.

With hydrochlorate of quinine a light yellow precipitate is first obtained, which becomes of a darker colour and crystalline when agitated. The solutions should not be too dilute.

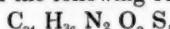
Hydrochlorate of cinchonine yields a yellow precipitate consisting of fine needles. Brucine, morphine and codeine produce crystalline compounds after some time, which are decomposed with the same facility as the hydroferrocyanates. Their aqueous solutions cannot be evaporated in vacuo over sulphuric acid, without decomposition.

The following formulæ have been deduced from the analyses of these compounds :



*On two derivatives of morphine and narcotine.\**—Messrs. Laurent and Gerhardt have investigated the substance obtained by the action of an excess of sulphuric acid upon morphine, which was first described by M. Arppe, in 1845, and to which the formula  $4(C_{35}H_{40}N_2O_6) + 5SO_3$  was assigned.

Starting with the supposition that the composition of this body, which is called *sulphomorphide*, must be analogous to those of the amides and anilides, they prepared it upon the plan proposed by M. Arppe, and found it to be a fixed persistent body, white when first prepared, but gradually becoming green, leaving a voluminous coal when burnt on a platinum blade. The analysis yielded the following relations :



which corresponds with the neutral sulphate of morphine, less 2 equivalents of water :



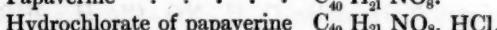
A similar substance, *sulphonarcotide*, is obtained by the action of sulphuric acid on narcotine, which has the composition expressed by the formula :



These bodies, sulphomorphide and sulphonarcotide, evidently belong to the same class as the amides and anilides ; they are to the sulphates of morphine and narcotine, what sulphamide and sulphanilide are to the neutral sulphates of ammonia and aniline. It is not possible again to obtain morphine and narcotine from them ; but it must be borne in mind, that in the case of the anilides, this is only possible with the aid of a high temperature, which of necessity decomposes the non-volatile bases, morphine and narcotine.

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*On a new organic base in opium.†*—Opium appears inexhaustible as a source of organic bases : to the five already known, Merck has now added a sixth, which he has discovered in the residues from the preparation of the compounds of morphine. The pure base, which Merck calls *papaverine*, is obtained in crystals from alcohol, in which it dissolves at a high temperature, and separates on cooling. Papaverine is little soluble in ether, and insoluble in water. Papaverine forms difficultly soluble salts with most acids ; the hydrochlorate is most easily obtained in the crystalline form. The author has analyzed the base, its compound with hydrochloric acid, and its double salt with platinum, the following are the results :



A full description of this new body and its combinations, the author reserves for a future communication.

\* Ann. de Chim. et de Phy. xxiv. 112.

† Ann. der Chem. und Pharm. lxvi, 125.

*On pectin, or the gelatinous principle of vegetables.*—The composition and chemical properties of pectin, which was first shewn to exist in a great variety of vegetable productions, by Vauquelin and Braconnot, have given rise to great diversity of opinion among modern chemists, and the substance has been analysed with very different results by Mulder, Regnault, Fremy, Fromberg, and Chodnew. It was supposed to exist (in company with pectinic acid) ready formed, and in the largest quantity, in the fruit and in the root of different plants, from which it was extracted by boiling water, and precipitated from the aqueous solution by alcohol. Boiled with weak hydrochloric acid it gives rise, according to Chodnew, to the formation of sugar and an acid, but this statement is in contradiction to the former experiments of Fremy; while the latter chemist has shewn that pectin is converted, by a solution of vegetable albumen, into pectic acid, and by potash and soda, or the carbonates of these alkalies, into pectic and metaplectic acids. Fremy has repeated and extended his researches upon the entire class of gelatinous vegetable principles, in a memoir, "On the ripening of fruits," with the following results.

The tissues of vegetables, and more particularly the fruits and roots, are found to contain a substance which is insoluble in water, and which it is proposed to call *pectose*; the characteristic property of this substance is, that it becomes converted into pectin by the action of the weakest acids. Pectose essentially differs from cellulose in all its properties.

Pectin, itself, exists in the juices of ripe fruits; it can be obtained artificially, by submitting pectose to the action of slightly acidulated liquids at the boiling temperature. Pectin is a weak acid; it causes no precipitation in neutral acetate of lead, and is converted into pectic acid under the influence of soluble bases. Pectin is precipitated from an aqueous solution by alcohol; but it often contains, when thus precipitated, dextrin, malate of lime, an albuminous matter, some compound of pectic acid, and some salts of ammonia; and if sulphuric or oxalic acids have been employed in its preparation, these acids form compounds with the pectin, which are precipitated under the same circumstances. This substance is more easily purified from the foreign matters which accompany its precipitation, when it is obtained from the juices of ripe fruits. The juice is expressed in the cold and filtered, the lime which exists in the juice being removed by oxalic acid, and the albuminous matter by a concentrated solution of tannin. The liquid is then treated with alcohol, which precipitates the pectin in long gelatinous filaments; it is washed with alcohol, dissolved in cold water, and again precipitated with alcohol. This operation is repeated three or four times, until reagents no longer indicate the presence of sugar, or of organic acids in the liquid. Pectin thus prepared leaves, on incineration, about 1 per cent of ash. As a test of its purity, the solution of pectin should be precipitated with hydrate of barytes, with which the pectin forms an insoluble pectate of barytes. The liquid filtered from this compound, and evaporated to dryness, should exhibit no traces of organic matter. When pure and unmixed with parapectin, it does not precipitate

the neutral acetate of lead, but forms an abundant precipitate with the basic acetate.

The composition of pectin is represented by the formula :



When pectin is submitted for a certain period to the action of boiling water, it acquires the property of precipitating the neutral acetate of lead, and is transformed into a new substance, which the author calls *parapectin*. This substance is neutral towards vegetable colouring matters; and is present in fruits which have attained a full state of ripeness. The composition of parapectin, dried at 100° C. (212° F.), is precisely similar to that of pectin; but when dried at 140° C. (284° F.), it is expressed by the formula :



Parapectin forms two compounds with oxide of lead.

Parapectin is converted, by the agency of acids, into *metapectin*, which exhibits a feeble acid reaction; it reddens the blue colour of litmus, and precipitates chloride of barium, and might consequently be called *metapectinic acid*. The composition of metapectin is precisely the same as that of pectin and parapectin.

The preceding substances produce soluble compounds with a certain number of acids, and principally with sulphuric and oxalic acids. These compounds are not crystallizable, and are precipitated in the form of a jelly, by alcohol.

Another substance is also found associated with pectose in the cellular tissue of plants, to which the author has given the name of *pectase*, and which possesses the property of transforming pectin successively into two gelatinous acids. This transformation is effected in the absence of air, and without any evolution of gas, constituting the pectic fermentation, which may be aptly compared to the lactic fermentation. Pectase exists in two modifications in the cellular tissue of vegetables: in a soluble, and in an insoluble state. Roots, like the carrot and beet-root, contain soluble pectase, and their juice gives rise to the pectic fermentation, while the juice of apples, and other acid fruits, is incapable of acting upon pectin. Pectase is contained in these fruits in the insoluble modification, and accompanies the insoluble portion of the pulp: when this pulp, however, is placed in a solution of pectin, the solution becomes rapidly gelatinous, and then contains two gelatinous acids. Soluble pectase is converted into the insoluble modification by coagulating it with alcohol.

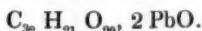
When pectin is subjected to the action of pectase, the first acid which is produced is the *pectosic*; this acid differs from pectic acid, in being perfectly soluble in boiling water. The acid is gelatinous, scarcely soluble in cold water, and becomes perfectly insoluble in the presence of acids; its solution in boiling water becomes gelatinous on cooling.

Pectosic acid is converted into pectic acid by the prolonged action of pectase, by boiling water, or by an excess of alkali. Both pectosic and

pectic acids are produced also, when pectine is acted on by lime, barytes, or strontian. The composition of the acid is represented by the following formula :



In the compound of the acid with oxide of lead, two atoms of water are replaced by two atoms of the metallic oxide :



The barytes compound is represented by the formula :



Pectic acid was discovered and described by Braconnot. It is formed by the action of pectase upon pectin, passing through the intermediate stage of pectonic acid. The usual mode of preparing this acid is, to submit the root containing pectin and pectase, in the state of pulp, to the action of a dilute solution of a carbonated alkali, the pectase is thus converted into a pectate of the alkali, which is then decomposed by hydrochloric acid, and the pectic acid thus separated. This acid is insoluble in cold water, and but little soluble in the same solvent at the boiling temperature, being converted, by continued boiling, into a new deliquescent acid, the *parapectic acid*. An excess of alkali must also be avoided in preparing the acid, or it becomes converted into *metapectic acid*. The composition of the acid is expressed by the formula :

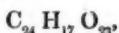


the elements of 2 atoms of water being replaced by 2 atoms of base in the salts.

Pectic acid is dissolved in considerable quantity in the neutral salts of the alkalies, and also in the ammoniacal salts of organic acids; it then forms double salts of a gelatinous nature and acid reaction, which are precipitated in the form of a jelly by alcohol.

Pectic acid is dissolved completely by the prolonged action of boiling water, and converted into a new acid—the *parapectic acid*, which is not crystallizable, possesses a distinctly acid reaction, and forms soluble salts with potash, soda, and ammonia; this acid is precipitated from solution by an excess of hydrate of barytes.

Parapectic acid is composed of :



the elements of 2 atoms of water being replaced by 2 atoms of base in its salts.

If the action of water is still longer prolonged upon pectic, or parapectic acids, they become converted into a very energetic acid, the *metapectic acid*, which is also produced under the following circumstances :

1. When a solution of pectin is left to itself for several days; the conversion is more rapid when pectose is present.
2. When pectin is submitted to the action of powerful acids, like hydrochloric acid, and boiled for a few minutes.

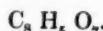
3. When pectin is treated with an excess of potash, or soda, it becomes converted into metapectate of the alkali. This is also the case with pectosic and pectic acids.

4. When pectic acid is allowed to stand in water for several months.

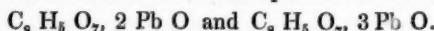
Metapectic acid is soluble in water, but is not crystallizable, it forms soluble salts with all the bases; its salts acquire a yellow colour under the influence of an excess of base. This acid is precipitated by basic acetate of lead.

Both perapectic and metapectic acids possess the property of decomposing, with the aid of a boiling temperature, the double tartrate of potash and copper, as is likewise the case with glucose.

The composition of metapectic acid is represented by the formula:



Two salts of lead, the one containing 2 and the other 3 atoms of base, have been produced with this acid, which present the formulæ:



These gelatinous substances evolve water and carbonic acid when exposed to a temperature of 200° C. (392° F.), and are converted into a pyrogenous acid, of a black colour, which the author calls *pyropectic* acid. This acid is insoluble in water, and forms uncrystallizable salts of a brown colour. The acid has the following composition:



The compositions of the substances investigated in the foregoing paper and of their lead-salts are collected in the following table:

Names of the gelatinous substances.	Composition of the gelatinous bodies.	Composition of their salts of lead.	Oxide of lead contained in 100 parts of the salt.
Pectose . . .	. . .	. . .	..
Pectin . . .	C <sub>64</sub> H <sub>40</sub> O <sub>56</sub> , 8 HO	. . .	..
Parapectin . . .	C <sub>64</sub> H <sub>40</sub> O <sub>56</sub> , 8 HO	C <sub>64</sub> H <sub>40</sub> O <sub>56</sub> , 7 HO, Pb O	10.6
Melapectin . . .	C <sub>64</sub> H <sub>40</sub> O <sub>56</sub> , 8 HO	C <sub>64</sub> H <sub>40</sub> O <sub>56</sub> , 6 HO, 2 Pb O	19.4
Pectosic acid . . .	C <sub>32</sub> H <sub>20</sub> O <sub>28</sub> , 3 HO	C <sub>32</sub> H <sub>20</sub> O <sub>28</sub> , HO, 2 Pb O	33.4
Pectic acid . . .	C <sub>32</sub> H <sub>20</sub> O <sub>28</sub> , 2 HO	C <sub>32</sub> H <sub>20</sub> O <sub>28</sub> , 2 Pb O	33.8
Perapectic acid . . .	C <sub>24</sub> H <sub>15</sub> O <sub>21</sub> , 2 HO	C <sub>24</sub> H <sub>15</sub> O <sub>21</sub> , 2 Pb O	40.5
Melapectic acid . . .	C <sub>8</sub> H <sub>5</sub> O <sub>7</sub> , 2 HO	C <sub>8</sub> H <sub>5</sub> O <sub>7</sub> , 2 Pb O	67.2
Pyropectic acid . . .	C <sub>14</sub> H <sub>9</sub> O <sub>9</sub>	. . .	..

The gelatinous substances of vegetables present all the generic characters of acids; their capacity of saturation and their energy increase in proportion as their constitution differs from that of pectose; they appear to be all derived from a ternary molecule C<sub>8</sub>H<sub>5</sub>O<sub>7</sub>, and only differ from each other in the proportions of water which they contain.

The properties of these gelatinous bodies enable us to explain the changes which a fruit undergoes when submitted to the action of heat, and

also the formation of the vegetable jellies. Vegetable jelly may be produced, firstly, by the transformation of pectin into pectosic and peptic acids by the agency of pectase; secondly, by the combination of peptic acid with the organic salts contained in the fruits.

Pectose, which is contained in the unripe fruits, is successively converted during ripening, into pectin, metapectin, and metapectic acid; these changes being produced by the action of acids and of pectase.

It has thus been shown, that the gelatinous bodies of vegetables undergo precisely the same changes under the influence of reagents, which they actually suffer during the progress of vegetation.

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*On vegetable principles.\**—M. Lebourgdais recommends the use of animal charcoal as a means of detaching the vegetable principles from aqueous solution. The decoctions are, in most cases, precipitated in the first instance by acetate of lead, and the filtered liquid is then agitated with animal charcoal; the charcoal having been washed and dried, is treated with alcohol, to which it again resigns the principle which it had taken up. In this manner M. Lebourgdais states that he has extracted digitalin, ilicin, scillitin, arnicin, columbin, colocynthin, and other vegetable principles.

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*On a means of removing the acid from stored wines.†*—When, after fermentation has taken place, new wine is stored away in casks, a certain proportion evaporates through the substance of the cask, and this quantity must be supplied at intervals, or the contents of the casks would be liable to spoil. With each fresh addition of wine, a certain portion of free tartaric acid is introduced, which, after a certain time, dissolves a portion of the acid tartrate of potash that lines the inside of the casks, and the wine is rendered acid. Liebig proposes the use of neutral tartrate of potash to correct this acidity, which forming with the free acid, an acid salt renders it insoluble, and precipitates, at the same time, all the bitartrate which had previously been held in solution by the acid. Carbonate of potash is not so applicable, as it remains dissolved in the wine as a neutral tartrate, which gives a peculiar disagreeable flavour, easily distinguished by connoisseurs.

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*Examination of the bile of the ox.‡*—In a former publication, Dr. Strecker§ endeavoured to prove that the bile of the ox was chiefly composed of the soda-salts of two acids; the one, cholic acid, nitrogenous, but containing no sulphur; the other, choleic acid, comprising both nitrogen and sulphur amongst its elements. Prosecuting these investigations, the same chemist now shows that these two acids, in combination with soda, form the sole

\* Ann. de Chim. et de Phys. xxiv. 58.

† Ann. der Chem. und Pharm. LXV. 352.

‡ Ann. der Chem. und Pharm. LXVII. 1.

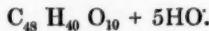
§ Ann. der Chem. und Pharm. LXV. 1, and Journ. of Chem. Soc. Vol. 1, p. 92.

constituents of that portion of purified ox-bile, which is soluble in alcohol and precipitated by ether, and consequently together form far the greater portion of the biliary secretion.

These facts have been deduced in great part from the study of the products of decomposition of cholic and choleic acids.

1. *Products of decomposition of choic acid.*—The cholic acid formerly described by the author is converted by the action of alkalies and by barytes into cholalic acid and glycicoll. When a solution of the acid is boiled for about twelve hours with an excess of hydrate of barytes, the volatile products being so condensed that they can flow back into the boiling liquid, a small quantity of ammonia and an oily substance are evolved, which are products of the decomposition of glycicoll; on cooling the solution, solidification ensues, the solid portion consisting of hydrate and cholalate of barytes. This product is washed with cold water and decomposed with hydrochloric acid, when the cholalic acid separates in the form of a resin. Dissolved in boiling alcohol, it is deposited, on cooling, in white tetrahedral, or more rarely octahedral crystals, of a vitreous lustre, which become dull on the surface by exposure to air, from the loss of water of crystallization. The crystals have a bitter taste, which becomes afterwards slightly sweet; they require 750 parts of boiling and 4000 parts of cold water for solution; 1000 parts of cold alcohol, of 70 per cent, retain 48 parts of dry cholalic acid in solution; in boiling alcohol the acid is much more soluble. On the addition of water to the alcoholic solution, the latter becomes turbid, and when allowed to remain at rest, deposits needle-shaped crystals of great brilliancy, mixed with others of a tetrahedral form. One part of cholalic acid requires 27 parts of ether for solution; by spontaneous evaporation the etherial solution deposits crystals which do not effloresce when exposed to the air.

The tetrahedral and octohedral crystals lose the whole of their water of crystallization at 100° C. (212° F.), but to dehydrate one gramme of the acid several days are requisite. The dry acid may be heated to 150° C. (302° F.) without loss of weight. Analysis yielded the following formula for the crystals belonging to the quadratic system:



The crystals deposited from an etherial solution belong to the rhombic system, and contain only two atoms of water, one of which they retain at a temperature of 100° C. (212° F.). The same quantity of water was found in the needles precipitated by water from an alcoholic solution, one equiv. being expelled at 100° C. (212° F.) and the other at 140° C. (284° F.). These differences in the relations of the acids to water might give rise to the supposition that they themselves were distinct, were not this controverted by the fact, that the one modification may be converted into the other by attention to the solvent employed and to the mode of obtaining the crystals. They must therefore be considered as modifications of the

same acid, and appear to correspond with the varieties of cholic acid previously observed by the author, and described as cholic, paracholic, and amorphous cholic acids.

Cholalic acid expels carbonic acid from the carbonate of the alkalies, and also dissolves in the caustic alkalies, forming crystalline salts, when the neutral solutions are evaporated by the application of heat. Insoluble salts of many metallic oxides may be obtained from these salts by double decomposition.

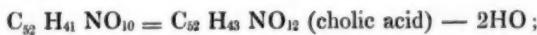
All the salts of cholalic acid are soluble in alcohol; they possess a bitter taste, which is slightly sweet. Heated with a solution of sugar and concentrated sulphuric acid, they exhibit the same violet colour as the salts of cholic acid. The cholalates of potash, ammonia, barytes, lime and silver were examined and described by the author.

When cholalic acid had been separated from the barytic solution by hydrochloric acid, the whole of the barytes was precipitated from the solution by sulphuric acid, and the clear solution was then boiled with hydrated oxide of lead which removed the hydrochloric and sulphuric acids. A large quantity of oxide of lead was however held in solution, and this was separated by sulphuretted hydrogen. The filtered liquid then deposited prismatic crystals, which corresponded in form, taste, and in all other properties with glycicoll. The analysis likewise confirmed this identity.

The reaction is therefore represented by the following formulae:

Cholic acid . . . . .	C <sub>52</sub> H <sub>48</sub> NO <sub>12</sub>
Cholalic acid . . . . .	C <sub>48</sub> H <sub>40</sub> O <sub>10</sub>
Difference . . . . .	C <sub>4</sub> H <sub>3</sub> NO <sub>2</sub>
With the addition of water . . . . .	H <sub>2</sub> O <sub>2</sub>
Glycicoll . . . . .	C <sub>4</sub> H <sub>5</sub> NO <sub>4</sub>

2. *Products of the decomposition of cholic acid by acids.*—When cholic acid is treated with concentrated hydrochloric or sulphuric acid, it is rapidly dissolved in the cold, and is again deposited on the addition of water. If the solution, however, be heated to the boiling point, it soon becomes turbid, and oily drops separate, which become solid and resinous when the liquid cools. A small quantity of a resinous body and a little hydrochlorate of glycicoll only are found in solution. The resinous body possesses the properties of a weak acid, but is not constant in composition, and the analysis of portions taken at different periods of the process, and of the barytes compounds produced from them, shewed that the action of hydrochloric acid consisted in a gradual elimination of the elements of water from the cholic acid. The first action of strong hydrochloric acid separates two atoms of water, leaving a substance of the following composition :



two further atoms of water are then separated, and there remains a body composed of



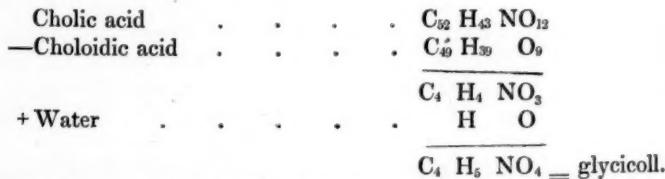
If cholic acid is boiled with water, and the process is continued after the separation of the resinous body, the latter undergoes further decomposition. It becomes gradually hard, and no longer melts in the liquid. The analysis of successive portions showed a constant increase in the amount of carbon until it attained 77 per cent, when no further increase was observed. Its solubility in alcohol diminishes in the same ratio, and the last product is no longer soluble in cold alcohol, while its solubility in ether is proportionally augmented. Amongst these different products the author has ascertained two only that are well defined. The one is an acid containing no nitrogen, the choloic acid of Demarçay, and the other the final product, is identical with the dyslysin of Berzelius.

The composition of the former is expressed by the formula  $\text{C}_{48} \text{H}_{39} \text{O}_9$ .

That of the latter by the formula  $\text{C}_{48} \text{H}_{36} \text{O}_6$ .

The choloic acid is anhydrous, and unites with bases without the separation of water, resembling, in this respect, hyocholinic acid. Its salts have the same composition as those of cholalic acid, but essentially different properties.

The acid liquid from which the choloic acid is separated contains a quantity of glycicoll, the production of which is explained in the following manner:



Dyslysin is obtained by boiling choloic acid with strong muriatic acid, and is reconverted into choloic acid by fusion with potash, or by boiling with an alcoholic solution of that base. The difference of composition between the two substances consisting in the elements of three equivs. of water.

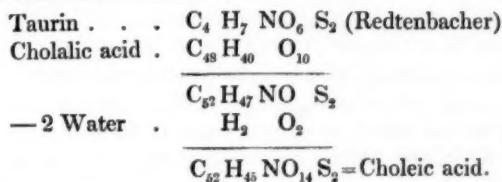
It was stated above, that the tetrahedral crystals of cholalic acid could be heated, when dry, to  $150^\circ \text{C}$ . ( $302^\circ \text{F}$ .) without loss of weight: at a temperature of  $195^\circ \text{C}$ . ( $383^\circ \text{F}$ .) however, they melt and lose from 22 to 24 per cent of water, and are then converted into choloic acid. One atom of water constituting the difference in the formulæ for the two acids. A higher temperature  $290^\circ \text{C}$ . ( $554^\circ \text{F}$ .) converts the acid into dyslysin, with the loss of 4 equivs. of water.

The prolonged action of powerful acids upon cholalic acid likewise converts it first into choloic acid, and subsequently into dyslysin.

3. *Choleic acid*.—In addition to cholic acid, obtained by precipitation with neutral acetate of lead, the bile likewise contains the soda salt of an acid, into the composition of which, both sulphur and nitrogen enter, and which acid is precipitated by the basic acetate of lead from the filtrate, separated from the cholate of lead. This acid is called choleic acid. The precipitate thus obtained by basic acetate of lead is not, however, of constantly uniform composition ; it consists of cholate and choleate of lead. As it was found difficult, if not impracticable, to separate these two acids completely from each other, an examination of the products of decomposition of the mixture of the salts of lead was resorted to, as a means of ascertaining the nature of choleic acid, the products of the decomposition of cholic acid having been previously investigated and established. The lead salts of the two acids were treated with hydrate of barytes, by which means the whole of the organic acids were rendered soluble and the greater portion of the lead was separated. This solution was boiled with an excess of hydrate of barytes for twenty-four hours, precisely in the same manner as was practised with cholic acid. The barytes being removed by a current of carbonic acid, a copious resinous precipitate was obtained by the addition of hydrochloric acid, which rapidly became hard and brittle. The filtrate was freed from barytes by sulphuric acid, and the sulphuric and hydrochloric acids by oxide of lead, which in its turn was removed by sulphuretted hydrogen. This liquid afforded on evaporation, taurin in considerable abundance, and likewise some glycicoll ; these were easily separated from each other by alcohol containing hydrochloric acid, in which solvent glycicoll is dissolved, but not taurin. These were the only products contained in the filtrate, with the exception of a very little cholalic acid, easily removable by ether.

The resinous body separated from the barytic solution by hydrochloric acid, was washed with water and dissolved in boiling alcohol. The solution deposited tetrahedral crystals of cholalic acid on cooling, and a further quantity was obtained by evaporation.

Cholalic acid, glycicoll, and taurin, are consequently the only products of the decomposition of the precipitate produced by basic acetate of lead in purified bile ; and as we know that the two former substances are the products of cholic acid, the taurin and a portion of cholalic acid must be derived from the other constituent of the bile, or from choleic acid. Choleic acid is, therefore, a conjugate cholalic acid, containing taurin as a conjunct, less two atoms of water, as is shown by the following known composition of its two constituents :



The author assumes 2 atoms of water less in the composition of choleic

acid than were actually found in the cholalic acid and taurin together, partly to establish its analogy to cholic acid, which likewise contains 2 atoms of water less than are present in cholalic acid and glycicoll together, and partly because choleic acid has no resemblance to a saline body, taurin not entering into combination, as such, with acids, and because the analysis of the mixture of the lead and other salts warrants such an assumption.

The formula for choleic acid being assumed as  $C_{62} H_{45} NO_{14} S_2$ , that of cholic acid was found to be  $C_{62} H_{48} NO_{12}$ .

The author has described the properties and reactions of the choleates at considerable length, and enters upon a comparison of his results with those obtained by former experimenters. The conclusions arrived at by this investigation may be summed up in the following manner.

The bile of the ox, in the fresh state, contains two principal ingredients, cholic and choleic acids, which are chiefly in combination with soda, and is not composed, as stated by Berzelius and Mulder, of an indifferent or neutral body, which in suffering decomposition, gives rise to ammonia, several acids, and taurin. The action of alkalies upon the bile is attended by the production of cholalic acid and glycicoll from the cholic acid, and of cholalic acid and taurin from the choleic acid. Acids give rise to the same soluble products, glycicoll and taurin, and at the same time, two insoluble substances are formed, choloïdic acid and dyslylin.

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*On the chemical constitution of cholesterin.\**—Zwenger has studied the action of sulphuric acid upon cholesterin and finds, that when concentrated sulphuric acid, mixed with half its volume of water, is allowed to act upon cholesterin at a temperature of from 60° to 70° C. (140° to 158° F.), more sulphuric acid being gradually added, until all the cholesterin has lost its crystalline character, and has become soft and of a dark red colour, the body is then converted into three new carbo-hydrogens, which, in combination with sulphuric acid, produce the red-coloured mass. No gas is evolved in this decomposition, and the mass only contains the three new bodies, with a little undecomposed cholesterin. The red colour disappears on the addition of water, and the product becomes white or yellowish. The sulphuric acid can be removed completely by repeated washing with water. The decomposed substance is now boiled with ether, which dissolves two of the new products, the third remaining insoluble. None of these bodies contain sulphur. The author proposes to designate all three by the term *cholesterolin*, with a distinguishing letter for each.

A Cholesterolin is the residue left by the ether, and is very little soluble in that liquid or in alcohol, and is quite insoluble in water. It is soluble in ethereal oils, and can be obtained crystalline from a solution in oil of turpentine. This substance is without smell or taste, and is lighter than water. It is difficultly fusible without decomposition at a temperature

\* Ann. der Chem. und Pharm. LXVI. 5.

of about 240° C. (464° F.). Analysis yielded, carbon 88·05, hydrogen 12·09.

*b* Cholesterin is obtained with *c* cholesterin from the etherial solution, by precipitation with alcohol, the alcohol holding the undecomposed cholesterin in solution. The yellow resinous precipitate, again treated with ether, leaves a small portion of *a* cholesterin undissolved, and by spontaneous evaporation, the *b* cholesterin is deposited in crystals, while *c* cholesterin is retained in solution, and obtained subsequently as a resinous body. By re-crystallization from ether, the *b* cholesterin may be purified.

*b* Cholesterin is insoluble in water, and nearly so in alcohol; warm ether dissolves it readily, and deposits it in white brilliant plates, or by slow evaporation, in white needles of great lustre. It is also soluble in fatty and etherial oils.

*b* Cholesterin melts at 255° C. (491° F.) and solidifies, on cooling, to a crystalline translucent mass. It is without taste or smell, and lighter than water. The analysis of this body yielded, carbon 88·29, hydrogen 12·18.

*c* Cholesterin is a yellow resinous body, which is deposited from the ether after the deposition of *b* cholesterin; it is purified by repeated solution in cold ether, and precipitation with alcohol, in which liquid it is insoluble. It cannot be obtained in a crystalline form, is without smell or taste, and lighter than water. Its melting point is about 127° C. (261° F.) and when cooled after fusion, it assumes the form of an amorphous, transparent, brittle body, of a yellowish tint. By sublimation it is converted into an etherial oil of an agreeable aromatic odour, but little carbon remaining. The analysis of this substance yielded, carbon 87·92, hydrogen 11·99.

The analyses of these bodies shew that they possess a very similar composition, and when considered as isomeric or polymeric, several formulae may be calculated for them, all of which, by the addition of the elements of water, may be made to correspond more or less closely with the composition of cholesterin. If they be viewed, however, as differently constituted, and composing, together with the elements of water, the compound body cholesterin, the formula for this latter substance may then be represented by the formula:



which perfectly coincides with the results of published analyses, and may be viewed in the following manner:



The three carbo-hydrogens in this equation yielding in 100 parts;

	$\text{C}_{32} \text{H}_{26}$	$\text{C}_{22} \text{H}_{18}$	$\text{C}_{27} \text{H}_{22}$
Carbon . .	88·07	88·00	88·04
Hydrogen . .	11·93	12·00	11·96
	100·00	100·00	100·00

Cholesterin may therefore be considered as the hydrate of a compound carbo-hydrogen, the water of which is separated by the agency of sulphuric acid, and the compound carbo-hydrogen itself resolved into three distinct carbo-hydrogens.

*On the quantitative estimation of urea.\**—Aqueous solutions of urea are easily decomposed into carbonate of ammonia when heated in hermetically closed vessels to a temperature above 100° C. (212° F.) This conversion commences at a temperature of 120° C. (248° F.), but proceeds slowly, until the temperature has risen to between 120° and 140° C. (248° to 284° F.) when it is completed in three or four hours. Bunsen having ascertained this fact, and found by direct experiment that hippuric and benzoic acids were not converted into carbonates under the same circumstances, that different mixtures of the most frequently occurring nitrogenous animal liquids and solids and the extractive matters of urine do not influence the final result of the process, or increase the amount of carbonate in an appreciable manner, has applied it to the quantitative estimation of the amount of urea in the urine in the following manner.

From 50 to 60 grammes of urine are weighed in a flask, the neck of which is slightly greased; the greater portion is then poured into another dry flask, and the amount poured off is determined by re-weighing the residue in the first vessel. This weighed portion of urine is then mixed with a concentrated solution of chloride of barium, to which a little ammonia has been added, the weight of the solution of chloride of barium being determined in the same manner. The uric acid is precipitated completely by the ammoniacal solution of chloride of barium, and must be separated prior to the application of heat. When the precipitate has therefore settled down in the corked flask, from 25 to 30 grains of the liquid are poured upon a dry filter and allowed to pass through a funnel with a long neck, drawn out to a point at the end, into a strong glass tube, closed at the bottom, and previously weighed, and which contains about 3 grammes of chemically pure solid chloride of barium. The long neck of the funnel allows of the upper part of the tube being kept dry, and when the weight of the liquid in the tube is accurately noted, the upper end is hermetically sealed by fusion with the blow-pipe at about 1 or 1½ inch from the level of the liquid; care being taken to thicken the glass where the juncture is effected.

The precipitate on the filter is washed in the meantime, and its weight determined.

The conversion of the urea into carbonate of ammonia is effected by exposing the hermetically sealed glass tube, surrounded by a closed copper tube, in a copper oil bath, heated by a lamp to a temperature between 220° and 240° C. (428°—464° F.) Glass tubes of 2·5 mm. thickness in the glass, and with an internal diameter of 15 mm., withstand the temperature without danger of explosion. After three or four hours' exposure,

\* Ann. der Chem. und Pharm. Lxv. 375.

the bath is allowed to cool, the glass tubes are cut with a file and cracked by a hot iron or piece of charcoal, and the crystals of carbonate of barytes are then collected on a filter, washed and weighed.

Every two equivs. of carbonate of barytes are equal to one equiv. of urea. A very slight error is occasioned by the sparing solubility of the carbonate of barytes in ammonia and sal-ammoniac; but this is compensated, at least in a degree, by the creatin contained in the urine, which under the circumstances, would also give rise to the production of a small quantity of carbonate of ammonia.

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*On the changes which organic substances suffer on their passage into the urine.\**—Messrs. Wöhler and Frerichs have caused a series of substances, of known composition, whose transformations under the action of re-agents are also well defined, to pass through the organs of different animals (dogs, rabbits, guinea-pigs, &c.), under favourable circumstances for collecting the excretion and observing the action of the different substances.

*Salicylous acid*, given with the food in doses of  $\frac{1}{2}$  to 4 grammes, was detected unchanged in the urine, not having been converted into hippuric acid, as might have been expected from its isomerism with benzoic acid.

*Oil of bitter almonds*, free from hydrocyanic acid, was not found to exert a poisonous action, as has been stated by other experimenters. The urine, after its administration, contained hippuric acid. It is therefore converted, by the addition of 2 atoms of oxygen, into benzoic acid, which is subsequently converted into hippuric acid.

*Amygdalin* is not poisonous; there is, therefore, no substance in the body which can perform the function of emulsion. In two cases only, when given in large doses, it produced drowsiness, from which the animals, however, soon recovered. The breath then gave off an odour of hydrocyanic acid. In other cases these symptoms were not observed, while the urine in all cases smelt strongly of the acid, when mixed with milk of almonds. A portion, therefore, of the amygdalin may have passed off by the kidneys.

*Benzoic ether* was traced as hippuric acid in the urine.

*Peruvian balsam* also afforded hippuric acid from the cinnamic acid which it contains, and another substance, which caused the urine to assume a blood-red colour with hydrochloric acid.

*Tannic acid* was converted into gallic acid, pyrogallic acid, and substances bearing a resemblance to humin.

*Urates and alantoin.* The normal quantity of urea was increased 5-fold in the urine of a rabbit by a dose of  $2\frac{1}{2}$  grammes of urate of potash.

Oxalate of lime was found in considerable quantity, with an increased amount of urea in the urine both of man and the dog, after having taken urate of potash.

\* Ann. der Chem. und Pharm. LXV. 335.

*Alantoin*, the other product of the decomposition of uric acid by peroxide of lead, was unsuccessfully sought in the urine.

*Alantoin*, given in considerable quantity, could not be detected in the urine, nor oxalate of ammonia, the product of its decomposition by boiling potash.

*Sulphocyanide of potassium* did not exhibit a poisonous action, as has been previously stated by other observers, but it appeared to diminish the activity of the spinal marrow. The sulphocyanide was always detected unchanged in the urine.

*Rhodallin*, or the combination of oil of mustard with ammonia, was found as sulphocyanide of ammonium in the urine. Oil of mustard is consequently decomposed in the body, in a similar manner as by soda-lime. What becomes of the allyle could not be ascertained.

*Chinon* was found to exert no poisonous action; but its decomposition could not be traced, nor was it found in the urine.

*Aniline* is not poisonous, nor was it present in the urine of the animals to which it was administered.

*Carbolic acid*, or hydrate of phenyle, acted as an energetic poison. It appears probable that this substance is one of the active principles in castoreum, and the study of its physiological action might possibly lead to the discovery of some substitute for that very expensive drug.

*Alloxantin*. This substance passed through the kidneys in considerable quantity; it did not appear to undergo any change into alloxan, but a more than normal quantity of urea was detected in the urine after its administration.

*Urea* was not converted into carbonate of ammonia, as was anticipated. The urine continued acid, and the urea probably passed off as such.

The authors find that arsenic acid is less poisonous than arsenious acid, and appears to undergo reduction to the state of arsenious acid in the gut. Arseniate of lime, lately discovered in many mineral waters, is also poisonous in large doses.

Pure phosphoric acid exerted no poisonous action whatever, whereas phosphorous acid caused death in every case that it was administered.

## TITLES OF CHEMICAL PAPERS

IN

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